Supporting Information

Substrate-directed divergent synthesis of fused indole polycycles through Rh(II)-catalyzed cascade reactions of bis(diazo)indolin-2-ones

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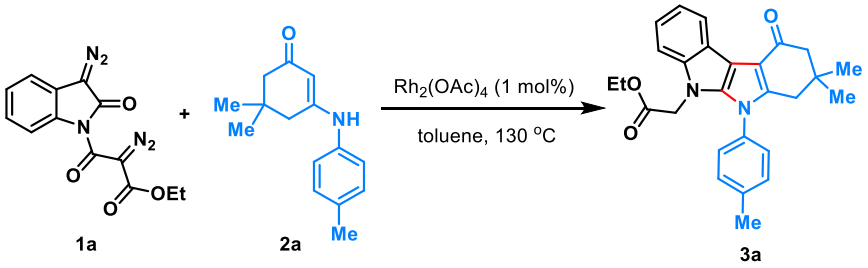
1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification. Bis(diazo)indolin-2-ones **1**,[1] enaminones **2**[2] and **4**[3] were prepared according to literature reports.

2. Optimization of conditions

Table S1. Optimization of condtions[a,b]

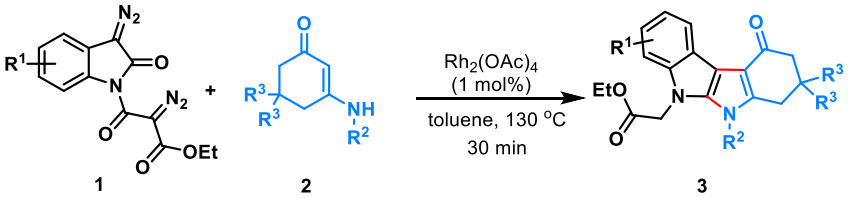


Entry	Ratio (**1a:2a**)	Time (h)	Yield (%)
1	1:1	0.5	55
2	1:1.2	0.5	50
3	1:1.5	0.5	44
4	1:1.8	0.5	47
5	1:2.0	0.5	38

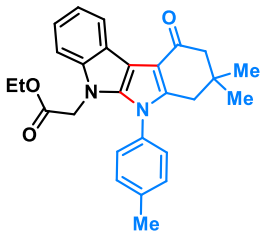
6	1.2:1	0.5	43
7	1.5:1	0.5	43
8	1:1	2	55
9	1:1	0.5	(45, 50)[c]

[a] Unless otherwise noted, the reactions were performed on a 0.20 mmol scale. [b] Isolated yields obtained by column chromatography. [c] 0.5 mL And 1.5 mL of toluene were used, respectively.

3. Experimental data for the formation of 3



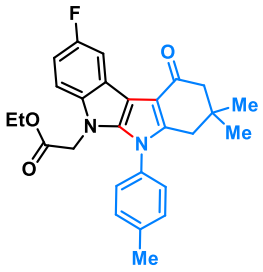
General procedure: To a 5.0 mL vial were successively added bis(diazo)indolin-2-ones **1** (0.20 mmol), cyclic enaminones **2** (0.20 mmol), $Rh_2(OAc)_4$ (0.002 mmol) and 1.0 mL of toluene. The resulting mixture was stirred at 130 °C for 30 min, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **3**.



Ethyl 2-(8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3a**)

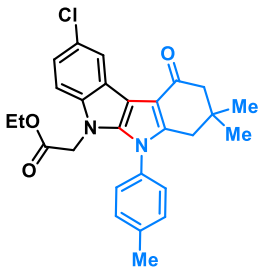
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 8:1); 46.7 mg, 55% yield; reaction time = 30 min; mp 164.1-164.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.0 Hz, 1H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 9.0 Hz, 2H), 7.13-7.02 (m, 3H), 4.34 (s, 2H), 3.95 (q, *J* = 6.0 Hz, 2H), 2.41-2.37 (m, 7H), 1.08-1.03 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 168.1, 143.8, 140.0, 139.7, 139.4, 133.0, 130.4, 127.6, 121.4, 121.2, 121.2, 120.3, 113.3, 108.4, 104.4, 61.4, 52.0, 45.0, 36.6, 35.8, 28.7, 21.2, 14.0. IR (KBr) *v* 3418, 2963, 1645, 1529, 1202, 1036, 741 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_3$ $[M+H]^+$ 429.2173, found

429.2173.



Ethyl 2-(2-fluoro-8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl) acetate (**3b**)

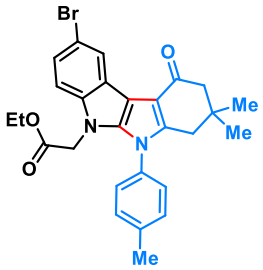
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 8:1); 33.3 mg, 37% yield; reaction time = 30 min; mp 197.0-197.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 6.99 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 7.88 (tt, $J_1 = J_2 = 4.0$ Hz, 1H), 4.40 (s, 2H), 4.04 (q, $J = 8.0$ Hz, 2H), 2.48 (s, 5H), 2.44 (s, 2H), 1.14 (t, $J = 8.0$ Hz, 3H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 168.0, 158.1 (d, $J = 233.0$ Hz, 1C), 144.2, 140.4, 139.9, 136.4, 132.7, 130.4, 127.6, 121.7 (d, $J = 11.0$ Hz, 1C), 113.1, 108.9 (d, $J = 10.0$ Hz, 1C), 108.6 (d, $J = 26.0$ Hz, 1C), 106.9 (d, $J = 25.0$ Hz, 1C), 104.3 (d, $J = 4.0$ Hz, 1C), 61.5, 51.8, 45.1, 36.5, 35.8, 28.6, 21.3, 14.0; ^{19}F NMR (375 MHz, $CDCl_3$) δ -123.7. IR (KBr) *v* 3469, 2965, 1746, 1639, 1524, 1208, 1032, 792 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{28}FN_2O_3$ $[M+H]^+$ 447.2078, found 447.2080.



Ethyl 2-(2-chloro-8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3c**)

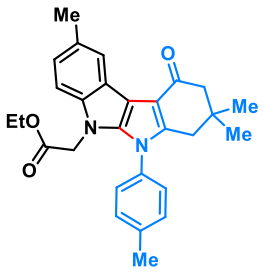
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 38.1 mg, 41% yield; reaction time = 30 min; mp 187.6-188.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, $J = 4.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.09 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 4.38 (s, 2H), 4.03 (q, $J = 8.0$ Hz, 2H), 2.47 (d, $J = 4.0$ Hz, 5H), 2.42 (s, 2H), 1.14 (t, $J = 8.0$ Hz, 3H), 1.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 167.8, 144.4,

140.0, 139.9, 138.3, 132.6, 130.4, 127.5, 125.8, 122.1, 121.0, 120.7, 113.1, 109.4, 103.8, 61.5, 51.8, 45.0, 36.4, 35.7, 28.6, 21.3, 14.0. IR (KBr) *v* 3440, 2928, 1747, 1641, 1526, 1438, 1208, 793 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{28}ClN_2O_3$ $[M+H]^+$ 463.1783, found 463.1780.



Ethyl 2-(2-bromo-8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3d**)

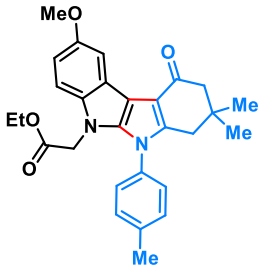
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 8:1); 35.9 mg, 35% yield; reaction time = 30 min; mp 210.7-211.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.21-7.17 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.33 (s, 2H), 3.97 (q, *J* = 8.0 Hz, 2H), 2.41 (s, 5H), 2.38 (s, 2H), 1.07 (t, *J* = 8.0 Hz, 3H), 1.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 167.8, 144.4, 140.0, 139.8, 138.7, 132.7, 130.5, 127.6, 123.8, 122.7, 113.5, 113.2, 109.9, 103.8, 61.6, 51.9, 45.1, 36.5, 35.8, 28.7, 21.3, 14.1, one carbon missing in the aromatic region. IR (KBr) *v* 3458, 2963, 1744, 1639, 1525, 1432, 796 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{28}BrN_2O_3$ $[M+H]^+$ 507.1278, found 507.1278.



Ethyl 2-(2,8,8-trimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3e**)

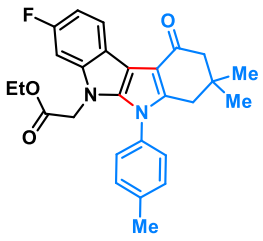
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 49.0 mg, 55% yield; reaction time = 30 min; mp 202.5-203.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 2H), 4.29 (s, 2H), 3.93 (q, *J* = 8.0 Hz, 2H), 2.40-2.35 (m, 10H), 1.04 (t, *J* = 8.0 Hz, 3H), 1.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 168.1, 143.7, 139.6, 138.4, 132.9, 130.3, 129.6, 127.5, 122.3, 121.3, 113.2, 108.0, 104.1,

61.2, 51.9, 45.0, 36.5, 35.7, 28.6, 21.3, 21.2, 14.0, two carbons missing in the aromatic region. IR (KBr) *v* 3424, 2920, 1752, 1640, 1526, 1201, 790 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_3$ $[M+H]^+$ 443.2329, found 443.2324.



Ethyl 2-(2-methoxy-8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3f**)

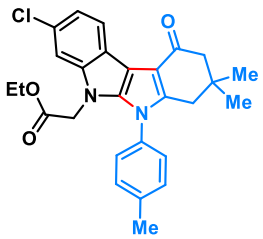
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1); 43.9 mg, 48% yield; reaction time = 30 min; mp 207.5-208.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 4.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.79 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.37 (s, 2H), 4.02 (q, *J* = 8.0 Hz, 2H), 3.92 (s, 3H), 2.47 (d, *J* = 4.0 Hz, 5H), 2.43 (s, 2H), 1.13 (t, *J* = 4.0 Hz, 3H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 168.1, 154.5, 143.9, 140.0, 139.6, 134.9, 132.8, 130.3, 127.5, 121.6, 113.1, 110.6, 109.2, 104.4, 103.7, 61.3, 55.8, 51.9, 45.1, 36.5, 35.7, 28.6, 21.2, 14.0. IR (KBr) *v* 3434, 2932, 1754, 1628, 1521, 1210, 792 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_4$ $[M+H]^+$ 459.2278, found 459.2275.



Ethyl 2-(3-fluoro-8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3g**)

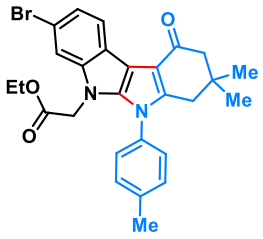
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 8:1); 32.4 mg, 36% yield; reaction time = 30 min; mp 204.8-205.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.94 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 6.80 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.35 (s, 2H), 4.05 (q, *J* = 8.0 Hz, 2H), 2.48 (s, 5H), 2.43 (s, 2H), 1.15 (t, *J* = 4.0 Hz, 3H), 1.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 167.8, 159.3 (d, *J* = 235.0 Hz, 1C), 143.7, 140.1 (d, *J* = 11.0 Hz, 1C), 139.8, 139.3, 132.8, 130.4,

127.5, 121.8 (d, J = 10.0 Hz, 1C), 117.7, 113.0, 108.1 (d, J = 23.0 Hz, 1C), 104.1, 95.8 (d, J = 27.0 Hz, 1C), 61.5, 51.9, 45.2, 36.4, 35.8, 28.6, 21.2, 14.0; ^{19}F NMR (375 MHz, $CDCl_3$) δ -120.7. IR (KBr) v 3448, 2963, 1639, 1523, 1205, 731 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{28}FN_2O_3$ $[M+H]^+$ 447.2078, found 447.2079.



Ethyl 2-(3-chloro-8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3h**)

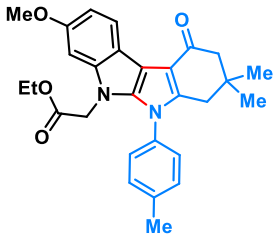
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 8:1); 33.5 mg, 36% yield; reaction time = 30 min; mp 219.1-219.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.17 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.09 (s, 1H), 4.37 (s, 2H), 4.05 (q, J = 8.0 Hz, 2H), 2.48 (s, 5H), 2.44 (s, 2H), 1.15 (t, J = 4.0 Hz, 3H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 167.7, 144.2, 140.3, 139.9, 139.5, 132.7, 130.4, 127.6, 126.7, 122.1, 120.8, 119.8, 113.1, 108.8, 104.1, 61.6, 51.9, 45.1, 36.5, 35.8, 28.7, 21.3, 14.0. IR (KBr) v 3466, 2960, 1745, 1643, 1524, 1207, 810 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{28}ClN_2O_3$ $[M+H]^+$ 463.1783, found 463.1783.



Ethyl 2-(3-bromo-8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3i**)

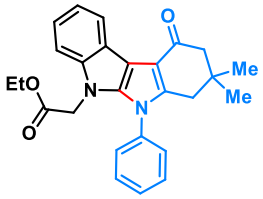
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 32.5 mg, 32% yield; reaction time = 30 min; mp 227.7-228.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.35-7.24 (m, 6H), 4.37 (s, 2H), 4.05 (q, J = 8.0 Hz, 2H), 2.47 (d, J = 4.0 Hz, 5H), 2.44 (s, 2H), 1.15 (t, J = 4.0 Hz, 3H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 167.7, 144.3, 140.6, 139.9, 139.4, 132.7, 130.4, 127.6, 123.4, 122.5, 120.1, 114.1, 113.1, 111.6, 104.2, 61.6, 51.9, 45.0, 36.5, 35.8, 28.7, 21.3, 14.0. IR (KBr) v 3433, 2960, 1745, 1639, 1523, 1206, 759

cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{28}BrN_2O_3$ $[M+H]^+$ 507.1278, found 507.1272.



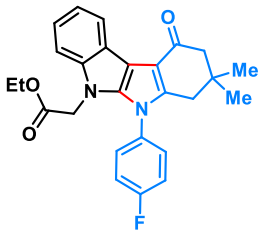
Ethyl 2-(3-methoxy-8,8-dimethyl-10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3j**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1); 40.5 mg, 44% yield; reaction time = 30 min; mp 216.2-217.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.77 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.54 (d, *J* = 4.0 Hz, 1H), 4.28 (s, 2H), 3.96 (q, *J* = 8.0 Hz, 2H), 3.75 (s, 3H), 2.39 (s, 5H), 2.35 (s, 2H), 1.06 (t, *J* = 4.0 Hz, 3H), 1.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 168.0, 155.8, 143.0, 140.9, 139.6, 138.8, 133.0, 130.3, 127.5, 121.8, 115.6, 113.0, 107.9, 104.2, 94.2, 61.3, 55.8, 51.9, 45.1, 36.5, 35.7, 28.6, 21.2, 14.0. IR (KBr) *v* 3453, 2952, 1744, 1641, 1525, 1462, 1211, 810 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_4$ $[M+H]^+$ 459.2278, found 459.2265.



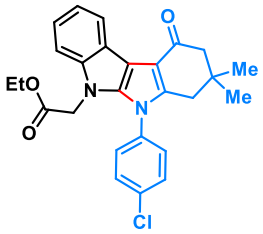
Ethyl 2-(8,8-dimethyl-10-oxo-6-phenyl-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3k**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 6:1); 38.8 mg, 47% yield; reaction time = 30 min; mp 193.2-193.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.46 (t, *J* = 4.0 Hz, 3H), 7.31 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 7.15-7.07 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 4.31 (s, 2H), 3.93 (q, *J* = 8.0 Hz, 2H), 2.37 (d, *J* = 20.0 Hz, 4H), 1.04 (t, *J* = 8.0 Hz, 3H), 1.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 168.0, 143.7, 140.0, 139.2, 135.6, 129.7, 129.5, 127.8, 121.3, 121.2, 121.1, 120.3, 113.3, 108.4, 104.5, 61.4, 51.9, 45.0, 36.5, 35.7, 28.6, 14.0. IR (KBr) *v* 3481, 2956, 1750, 1644, 1526, 1204, 736 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{27}N_2O_3$ $[M+H]^+$ 415.2016, found 415.2016.



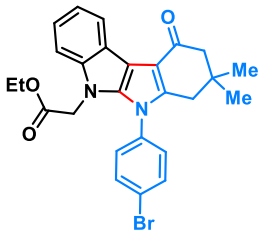
Ethyl 2-(6-(4-fluorophenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl) acetate (**3l**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 40.7 mg, 47% yield; reaction time = 30 min; mp 199.4-199.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.34-7.30 (m, 2H), 7.18-7.08 (m, 4H), 7.02 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.30 (s, 2H), 3.96 (q, *J* = 8.0 Hz, 2H), 2.33 (d, *J* = 12.0 Hz, 4H), 1.07 (t, *J* = 8.0 Hz, 3H), 1.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 168.0, 162.8 (d, *J* = 249.0 Hz, 1C), 143.7, 140.0, 139.2, 131.6 (d, *J* = 3.0 Hz, 1C), 129.8 (d, *J* = 8.0 Hz, 1C), 121.3 (d, *J* = 8.0 Hz, 1C), 121.1, 120.4, 116.9, 116.7, 113.4, 108.4, 104.5, 61.5, 51.8, 45.0, 36.4, 35.7, 28.6, 14.0; ^{19}F NMR (375 MHz, $CDCl_3$) δ -110.3. IR (KBr) *v* 3451, 2948, 1750, 1640, 1524, 1214, 1037, 740 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{26}FN_2O_3$ $[M+H]^+$ 433.1922, found 433.1920.



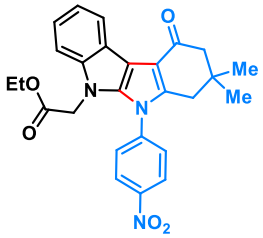
Ethyl 2-(6-(4-chlorophenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl) acetate (**3m**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 35.5 mg, 40% yield; reaction time = 30 min; mp 202.6-203.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.18-7.10 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.35 (s, 2H), 3.97 (q, *J* = 8.0 Hz, 2H), 2.36 (d, *J* = 12.0 Hz, 4H), 1.09 (t, *J* = 8.0 Hz, 3H), 1.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 168.0, 143.5, 140.0, 139.1, 135.6, 134.2, 130.0, 129.2, 121.5, 121.4, 121.1, 120.5, 113.7, 108.5, 104.8, 61.6, 51.9, 45.1, 36.5, 35.8, 28.6, 14.0. IR (KBr) *v* 3480, 2964, 1750, 1643, 1529, 1203, 1034, 740 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{26}ClN_2O_3$ $[M+H]^+$ 449.1626, found 449.1629.



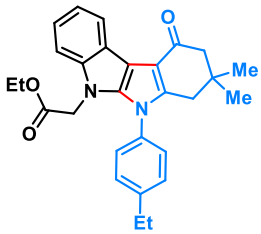
Ethyl 2-(6-(4-bromophenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl) acetate (**3n**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 8:1); 46.9 mg, 48% yield; reaction time = 30 min; mp 203.6-204.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 12.0 Hz, 2H), 7.16-7.09 (m, 2H), 7.03 (d, J = 8.0 Hz, 1H), 4.34 (s, 2H), 3.96 (q, J = 8.0 Hz, 2H), 2.35 (d, J = 16.0 Hz, 4H), 1.09 (t, J = 8.0 Hz, 3H), 1.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 168.0, 143.4, 140.0, 139.0, 134.7, 133.0, 129.5, 123.5, 121.4, 121.1, 120.5, 113.7, 108.5, 104.8, 61.6, 51.8, 45.1, 36.5, 35.7, 28.6, 14.1, one carbon missing in the aromatic region. IR (KBr) v 3480, 2964, 1751, 1644, 1530, 1202, 1034, 740 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{26}BrN_2O_3$ $[M+H]^+$ 493.1121, found 493.1121.



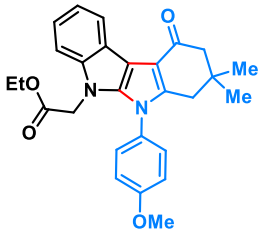
Ethyl 2-(8,8-dimethyl-6-(4-nitrophenyl)-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)a cetate (**3o**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1); 36.7 mg, 40% yield; reaction time = 30 min; mp 222.7-223.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.0 Hz, 2H), 8.14 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.19-7.14 (m, 2H), 7.08-7.06 (m, 1H), 4.37 (s, 2H), 3.99 (q, J = 8.0 Hz, 2H), 2.40 (d, J = 24.0 Hz, 4H), 1.08 (t, J = 8.0 Hz, 3H), 1.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 167.9, 147.7, 142.9, 141.5, 140.3, 138.7, 128.5, 125.1, 121.9, 121.6, 121.0, 120.9, 114.6, 108.7, 105.7, 61.8, 51.8, 45.5, 36.8, 35.9, 28.6, 14.1. IR (KBr) v 3428, 2962, 1751, 1636, 1527, 1343, 1202, 1038, 742 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{26}N_3O_5$ $[M+H]^+$ 460.1867, found 460.1859.



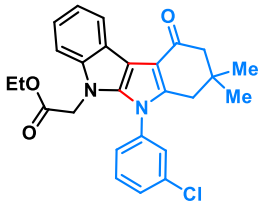
Ethyl 2-(6-(4-ethylphenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3p**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 45.9 mg, 52% yield; reaction time = 30 min; mp 173.2-173.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.30-7.03 (m, 7H), 4.36 (s, 2H), 3.96 (q, J = 8.0 Hz, 2H), 2.71 (q, J = 8.0 Hz, 2H), 2.42 (d, J = 16.0 Hz, 4H), 1.26 (t, J = 8.0 Hz, 3H), 1.09-0.97 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 168.1, 145.9, 143.9, 140.0, 139.4, 133.1, 129.1, 127.7, 121.4, 121.2, 121.2, 120.4, 113.3, 108.4, 104.4, 61.4, 52.0, 45.1, 36.6, 35.8, 28.7, 28.6, 15.3, 14.1. IR (KBr) ν 3438, 2962, 1749, 1642, 1526, 1203, 1040, 745 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_3$ $[M+H]^+$ 443.2329, found 443.2325.



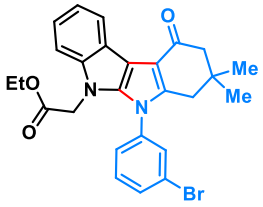
Ethyl 2-(6-(4-methoxyphenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3q**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1); 45.3 mg, 52% yield; reaction time = 30 min; mp 199.1-199.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.20-7.16 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 4.40 (s, 2H), 4.02 (q, J = 8.0 Hz, 2H), 3.88 (s, 3H), 2.43 (d, J = 16.0 Hz, 4H), 1.13 (t, J = 8.0 Hz, 3H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 168.1, 160.2, 144.1, 139.9, 139.4, 129.0, 127.9, 121.3, 121.2, 121.0, 120.2, 114.8, 113.1, 108.3, 104.1, 61.3, 55.6, 51.9, 44.9, 36.4, 35.7, 28.6, 14.0. IR (KBr) ν 3432, 2961, 1746, 1649, 1522, 1205, 1019, 748 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_4$ $[M+H]^+$ 445.2122, found 445.2116.



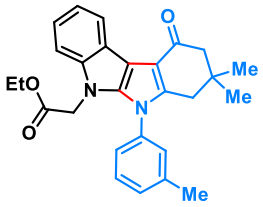
Ethyl 2-(6-(3-chlorophenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl) acetate (**3r**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 38.3 mg, 43% yield; reaction time = 30 min; mp 213.7-214.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.46-7.36 (m, 3H), 7.24 (d, J = 8.0 Hz, 1H), 7.14-7.07 (m, 2H), 7.01 (d, J = 4.0 Hz, 1H), 4.30 (d, J = 16.0 Hz, 2H), 3.98 (q, J = 8.0 Hz, 2H), 2.34 (d, J = 28.0 Hz, 4H), 1.08 (t, J = 8.0 Hz, 3H), 1.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 167.9, 143.4, 140.0, 138.9, 136.8, 135.3, 130.7, 129.7, 128.0, 126.1, 121.4, 121.4, 121.0, 120.4, 113.6, 108.5, 104.7, 61.6, 51.8, 45.1, 36.4, 35.7, 28.6, 14.0. IR (KBr) *v* 3486, 2944, 1751, 1636, 1583, 1197, 1038, 741 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{26}ClN_2O_3$ $[M+H]^+$ 449.1626, found 449.1612.



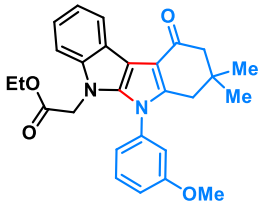
Ethyl 2-(6-(3-bromophenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl) acetate (**3s**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 38.6 mg, 39% yield; reaction time = 30 min; mp 221.4-222.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 4.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.22-7.17 (m, 2H), 7.11 (d, J = 8.0 Hz, 1H), 4.41 (d, J = 16.0 Hz, 2H), 4.08 (q, J = 8.0 Hz, 2H), 2.44 (d, J = 24.0 Hz, 4H), 1.17 (t, J = 8.0 Hz, 3H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 167.9, 143.4, 140.0, 139.0, 137.0, 132.7, 131.0, 130.8, 126.6, 123.1, 121.4, 121.0, 120.5, 113.7, 108.5, 104.7, 61.7, 51.8, 45.1, 36.5, 35.8, 28.6, 14.1, one carbon missing in the aromatic region. IR (KBr) *v* 3437, 2949, 1746, 1646, 1525, 1459, 1204, 1038, 744 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{26}BrN_2O_3$ $[M+H]^+$ 493.1121, found 493.1114.



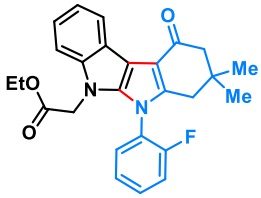
Ethyl 2-(8,8-dimethyl-10-oxo-6-(*m*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3t**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 40.7 mg, 48% yield; reaction time = 30 min; mp 178.0-178.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.14-7.07 (m, 4H), 7.02 (d, J = 8.0 Hz, 1H), 4.33 (s, 2H), 3.96 (q, J = 8.0 Hz, 2H), 2.42 (s, 2H), 2.36 (s, 5H), 1.06 (t, J = 8.0 Hz, 3H), 1.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 168.0, 143.7, 140.0, 139.2, 135.5, 130.2, 129.5, 128.2, 124.7, 121.3, 121.2, 121.1, 120.3, 113.3, 108.4, 104.4, 61.4, 51.9, 45.0, 36.5, 35.7, 28.6, 21.2, 14.0, one carbon missing in the aromatic region. IR (KBr) v 3456, 2954, 1746, 1648, 1524, 1454, 1206, 1026, 744 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_3$ $[M+H]^+$ 429.2173, found 429.2166.



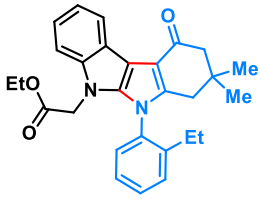
Ethyl 2-(6-(3-methoxyphenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3u**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1 to 5:1); 35.1 mg, 40% yield; reaction time = 30 min; mp 176.5-177.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.15-7.08 (m, 2H), 7.04-6.98 (m, 2H), 6.90 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.87 (t, J = 4.0 Hz, 1H), 4.36 (d, J = 4.0 Hz, 2H), 3.97 (q, J = 8.0 Hz, 2H), 3.78 (s, 3H), 2.40 (d, J = 36.0 Hz, 4H), 1.07 (t, J = 8.0 Hz, 3H), 1.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 168.1, 160.5, 143.6, 140.0, 139.2, 136.7, 130.5, 121.4, 121.2, 121.2, 120.3, 119.8, 115.0, 113.6, 113.4, 108.4, 104.5, 61.4, 55.5, 51.9, 45.1, 36.5, 35.7, 28.6, 14.0. IR (KBr) v 3450, 2956, 1748, 1648, 1600, 1525, 1205, 1028, 745 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_4$ $[M+H]^+$ 445.2122, found 445.2118.



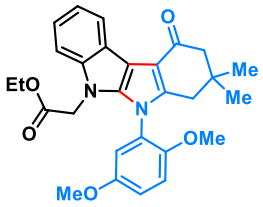
Ethyl 2-(6-(2-fluorophenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl) acetate (**3v**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 33.3 mg, 39% yield; reaction time = 30 min; mp 176.2-176.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.56 (q, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.23-7.18 (m, 2H), 7.15 (d, *J* = 4.0 Hz, 1H), 4.46 (d, *J* = 16.0 Hz, 2H), 3.99 (q, *J* = 8.0 Hz, 2H), 2.53-2.19 (m, 4H), 1.11 (q, *J* = 8.0 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 167.9, 158.1 (d, *J* = 251.0 Hz, 1C), 144.2, 139.9, 139.0, 131.6 (d, *J* = 28.0 Hz, 1C), 130.2, 125.1, 125.0, 123.4 (d, *J* = 13.0 Hz, 1C), 121.3 (d, *J* = 6.0 Hz, 1C), 121.1, 120.4, 117.1 (d, *J* = 19.0 Hz, 1C), 113.9, 108.5, 104.8, 61.5, 51.9, 44.9, 36.2, 35.8, 28.6 (d, *J* = 31.0 Hz, 1C), 14.0; ^{19}F NMR (375 MHz, $CDCl_3$) δ -119.5. IR (KBr) *v* 3441, 2962, 1748, 1644, 1527, 1204, 1038, 749 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{26}FN_2O_3$ $[M+H]^+$ 433.1922, found 433.1916.



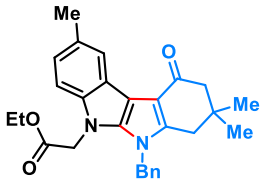
Ethyl 2-(6-(2-ethylphenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)a cetate (**3w**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 39.9 mg, 45% yield; reaction time = 30 min; mp 181.8-182.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.46 (tt, $J_1 = J_2$ = 8.0 Hz, 1H), 7.39 (d, *J* = 4.0 Hz, 1H), 7.28 (tt, $J_1 = J_2$ = 8.0 Hz, 1H), 7.23 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.17-7.08 (m, 2H), 7.03 (d, *J* = 4.0 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 4.09 (d, *J* = 16.0 Hz, 1H), 3.96-3.90 (m, 2H), 2.48-2.21 (m, 6H), 1.05-0.97 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 167.9, 143.6, 142.7, 140.0, 139.1, 133.8, 130.4, 129.5, 128.9, 127.1, 121.3, 121.3, 121.1, 120.4, 113.3, 108.5, 104.3, 61.4, 52.0, 44.6, 36.4, 35.8, 29.2, 28.1, 23.6, 14.0. IR (KBr) *v* 3450, 2951, 1750, 1648, 1525, 1203, 744 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_3$ $[M+H]^+$ 443.2329, found 443.2323.



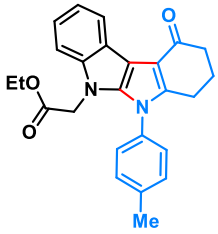
Ethyl 2-(6-(2,5-dimethoxyphenyl)-8,8-dimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3x**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1); 27.4 mg, 29% yield; reaction time = 30 min; mp 183.2-183.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.13-7.05 (m, 3H), 6.99-6.92 (m, 2H), 6.85 (d, J = 4.0 Hz, 1H), 4.48 (d, J = 16.0 Hz, 1H), 4.28 (d, J = 16.0 Hz, 1H), 3.96-3.91 (m, 2H), 3.71 (s, 3H), 3.60 (s, 3H), 2.46-2.31 (m, 4H), 1.05 (q, J = 4.0 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 168.1, 153.6, 149.7, 144.6, 139.9, 139.2, 124.4, 121.2, 121.2, 120.9, 120.1, 115.8, 115.5, 113.3, 108.4, 104.2, 99.9, 61.3, 56.2, 55.8, 52.0, 44.7, 36.3, 35.8, 29.0, 14.0. IR (KBr) *v* 3454, 2951, 1747, 1646, 1521, 1216, 1038, 741 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_5$ $[M+H]^+$ 475.2227, found 475.2223.



Ethyl 2-(6-benzyl-2,8,8-trimethyl-10-oxo-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3y**)

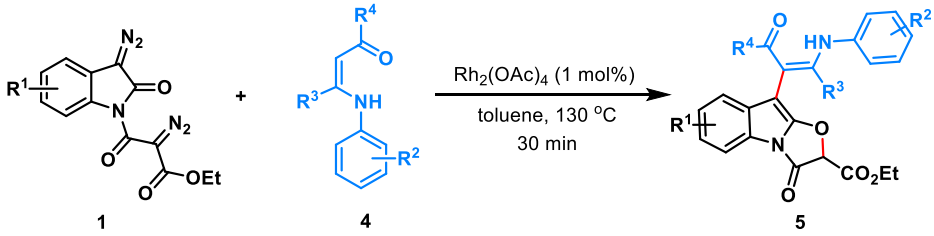
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 6:1); 16.1 mg, 18% yield; reaction time = 30 min; mp 204.1-205.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.33-7.28 (m, 3H), 7.04-6.95 (m, 4H), 5.30 (s, 2H), 4.56 (s, 2H), 4.02 (q, J = 8.0 Hz, 2H), 2.65 (s, 2H), 2.49 (s, 3H), 2.47 (s, 2H), 1.16-1.13 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 168.5, 142.9, 139.0, 138.6, 136.5, 129.7, 129.2, 128.0, 125.2, 122.4, 121.3, 121.1, 112.9, 108.2, 105.2, 61.6, 51.7, 47.3, 45.7, 36.0, 35.6, 28.7, 21.3, 14.0. IR (KBr) *v* 3062, 2950, 1745, 1637, 1208, 735 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_3$ $[M+H]^+$ 443.2335, found 443.2333.



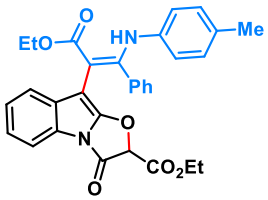
Ethyl 2-(10-oxo-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**3z**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 41.3 mg, 52% yield; reaction time = 30 min; mp 171.2-171.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 7.32-7.25 (m, 4H), 7.22-7.14 (m, 2H), 7.09 (d, $J = 4.0$ Hz, 1H), 4.40 (s, 2H), 4.01 (q, $J = 8.0$ Hz, 2H), 2.59 (tt, $J_1 = J_2 = 8.0$ Hz, 4H), 2.46 (s, 3H), 2.19-2.12 (m, 2H), 1.12 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 168.0, 145.0, 140.0, 139.6, 139.2, 132.9, 130.3, 127.5, 121.3, 121.2, 121.1, 120.2, 114.4, 108.4, 104.5, 61.3, 45.0, 37.8, 23.9, 22.5, 21.2, 14.0. IR (KBr) *v* 3485, 2941, 1752, 1635, 1529, 1201, 1013, 736 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{25}N_2O_3$ $[M+H]^+$ 401.1860, found 401.1857.

4. Experimental data for the formation of 5



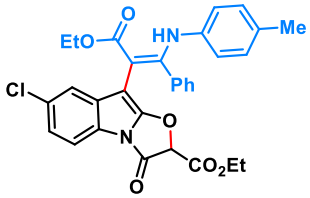
General procedure: To a 5.0 mL vial were successively added bis(diazo)indolin-2-ones **1** (0.20 mmol), acyclic enaminones **4** (0.20 mmol), $Rh_2(OAc)_4$ (0.002 mmol) and 1.0 mL of toluene. The resulting mixture was stirred at 130 °C for 30 min, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **5**.



Ethyl 9-(3-ethoxy-3-oxo-1-phenyl-1-(*p*-tolylamino)prop-1-en-2-yl)-3-oxo-2,3-dihydrooxazolo[3,2-*a*]indole-2-carboxylate (**5a**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 25:1); 72.1 mg, 69% yield; reaction time = 30 min; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.19-7.06 (m, 8H), 6.88 (d, J = 12.0 Hz, 2H), 6.61 (d, J = 12.0 Hz, 2H), 6.15-5.82 (m, 1H), 4.27 (q, J = 8.0 Hz, 2H), 4.14-3.96 (m, 2H), 2.13 (s, 3H), 1.25 (t, J = 8.0 Hz, 3H), 1.10 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.6, 163.2, 160.8, 159.6, 152.3, 137.1, 136.5,

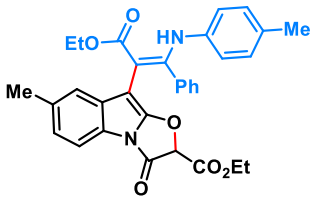
134.1, 132.7, 129.2, 128.7, 128.5, 127.6, 124.8, 124.2, 122.7, 121.9, 119.4, 112.0, 88.6, 86.3, 84.3, 62.6, 59.3, 20.2, 14.3, 13.9. IR (KBr) *v* 2982, 1763, 1600, 1464, 1267, 1132, 752 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{29}N_2O_6$ $[M+H]^+$ 525.2020, found 525.2020.



Ethyl

7-chloro-9-(3-ethoxy-3-oxo-1-phenyl-1-(*p*-tolylamino)prop-1-en-2-yl)-3-oxo-2,3-dihydrooxazolo[3,2-*a*]indole-2-carboxylate (**5b**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 50:1 to 45:1); 54.9 mg, 49% yield; reaction time = 30 min; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.23 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.08 (q, *J* = 8.0 Hz, 6H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.14-5.84 (m, 1H), 4.26 (q, *J* = 8.0 Hz, 2H), 4.15-4.05 (m, 2H), 2.14 (s, 3H), 1.24 (t, *J* = 8.0 Hz, 3H), 1.11 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.3, 162.8, 161.1, 159.5, 153.2, 138.0, 137.0, 134.0, 132.8, 129.3, 129.1, 128.8, 128.5, 127.6, 122.9, 122.6, 121.7, 119.2, 113.3, 88.6, 85.5, 84.4, 62.6, 59.3, 20.2, 14.3, 13.9. IR (KBr) *v* 3440, 1765, 1647, 745 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{28}ClN_2O_6$ $[M+H]^+$ 559.1630, found 559.1630.

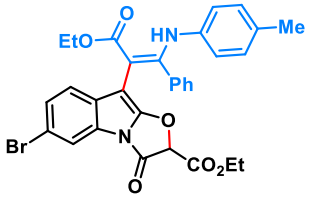


Ethyl

9-(3-ethoxy-3-oxo-1-phenyl-1-(*p*-tolylamino)prop-1-en-2-yl)-7-methyl-3-oxo-2,3-dihydrooxazolo[3,2-*a*]indole-2-carboxylate (**5c**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 50:1 to 40:1); 67.4 mg, 63% yield; reaction time = 30 min; mp 88.2-89.0 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.22 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.09-7.02 (m, 6H), 6.89 (d, *J* = 8.0 Hz, 3H), 6.62 (d, *J* = 8.0 Hz, 2H), 6.11-5.75 (m, 1H), 4.26 (q, *J* = 8.0 Hz, 2H), 4.14-4.04 (m, 2H), 2.30 (s, 3H), 2.14 (s, 3H), 1.24 (t, *J* = 8.0 Hz, 3H), 1.11 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.6, 163.2, 160.7, 159.6, 159.2, 137.1, 136.6, 134.1, 134.0, 132.7, 129.1, 128.7, 128.5, 127.6, 122.9,

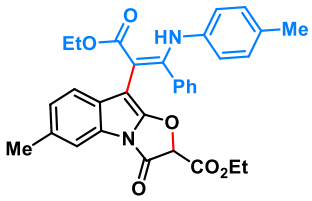
122.7, 122.3, 119.7, 111.6, 88.4, 86.5, 84.2, 62.5, 59.3, 21.3, 20.2, 14.3, 13.9. IR (KBr) *v* 3449, 1761, 1645, 703 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{31}N_2O_6$ $[M+H]^+$ 539.2177, found 539.2177.



Ethyl

6-bromo-9-(3-ethoxy-3-oxo-1-phenyl-1-(*p*-tolylamino)prop-1-en-2-yl)-3-oxo-2,3-dihydrooxazolo[3,2-*a*]indole-2-carboxylate (**5d**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 50:1 to 40:1); 70.7 mg, 59% yield; reaction time = 30 min; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.23 (d, *J* = 4.0 Hz, 1H), 7.64 (d, *J* = 4.0 Hz, 1H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.19 (d, *J* = 4.0 Hz, 1H), 7.06-7.05 (m, 5H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 6.15-5.84 (m, 1H), 4.27 (q, *J* = 8.0 Hz, 2H), 4.22-4.13 (m, 2H), 2.13 (s, 3H), 1.24 (t, *J* = 8.0 Hz, 3H), 1.10 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.4, 162.8, 161.1, 159.6, 152.4, 137.0, 135.6, 134.0, 132.8, 129.2, 128.8, 1285, 127.7, 127.6, 124.7, 122.8, 121.3, 114.6, 113.6, 88.6, 85.6, 84.4, 62.6, 59.4, 20.2, 14.3, 13.9. IR (KBr) *v* 3425, 1766, 1651, 998, 768 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{28}BrN_2O_6$ $[M+H]^+$ 603.1125, found 603.1124.

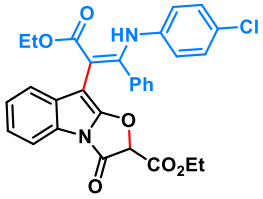


Ethyl

9-(3-ethoxy-3-oxo-1-phenyl-1-(*p*-tolylamino)prop-1-en-2-yl)-6-methyl-3-oxo-2,3-dihydrooxazolo[3,2-*a*]indole-2-carboxylate (**5e**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 50:1 to 40:1); 54.3 mg, 50% yield; reaction time = 30 min; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 7.12-7.03 (m, 7H), 6.88 (d, *J* = 12.0 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 12.0 Hz, 2H), 6.08-5.72 (m, 1H), 4.26 (q, *J* = 8.0 Hz, 2H), 4.14-4.04 (m, 2H), 3.34 (s, 3H), 2.13 (s, 3H), 1.24 (t, *J* = 8.0 Hz, 3H), 1.10 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.6, 163.2, 160.7, 159.6, 155.4, 150.9, 137.1, 134.1, 132.7, 129.6, 129.2, 128.7, 128.5, 127.6, 124.6, 122.7, 120.2,

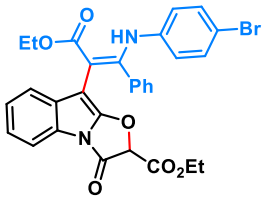
112.5, 97.5, 88.1, 86.5, 84.1, 62.5, 59.3, 55.4, 20.2, 14.3, 13.9. IR (KBr) *v* 3428, 1646, 996, 766 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{31}N_2O_6$ $[M+H]^+$ 539.2177, found 539.2177.



Ethyl

9-(1-((4-chlorophenyl)amino)-3-ethoxy-3-oxo-1-phenylprop-1-en-2-yl)-3-oxo-2,3-dihydrooxazolo [3,2-*a*]indole-2-carboxylate (**5f**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 50:1 to 40:1); 58.6 mg, 54% yield; reaction time = 30 min; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.13 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.22-7.05 (m, 10H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.18-5.74 (m, 1H), 4.27 (q, *J* = 8.0 Hz, 2H), 4.14-4.10 (m, 2H), 1.25 (t, *J* = 8.0 Hz, 3H), 1.10 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.3, 163.1, 159.6, 159.5, 152.2, 138.9, 136.3, 133.9, 129.0, 128.6, 128.5, 127.8, 127.4, 124.8, 124.2, 124.0, 121.9, 119.5, 112.0, 88.4, 88.3, 84.3, 62.6, 59.5, 14.3, 13.9. IR (KBr) *v* 3446, 1761, 1640, 1231 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{26}ClN_2O_6$ $[M+H]^+$ 545.1474, found 545.1474.

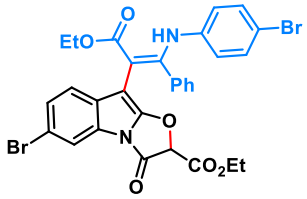


Ethyl

9-(1-((4-bromophenyl)amino)-3-ethoxy-3-oxo-1-phenylprop-1-en-2-yl)-3-oxo-2,3-dihydrooxazolo [3,2-*a*]indole-2-carboxylate (**5g**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 50:1 to 40:1); 61.5 mg, 52% yield; reaction time = 30 min; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.22-7.05 (m, 8H), 6.67 (d, *J* = 8.0 Hz, 2H), 6.23-5.75 (m, 1H), 4.27 (q, *J* = 8.0 Hz, 2H), 4.17-4.11 (m, 2H), 1.25 (t, *J* = 8.0 Hz, 3H), 1.10 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.3, 163.1, 159.5, 159.5, 152.1, 139.3, 136.2, 133.9, 131.4, 129.0, 128.6, 127.8, 124.8, 124.3, 124.2, 121.9, 119.5, 115.4, 112.0, 88.5, 88.4, 84.3, 62.6, 59.5, 14.2, 13.9. IR (KBr) *v* 3427, 1648, 996, 765 cm^{-1}. HRMS (ESI) calcd for

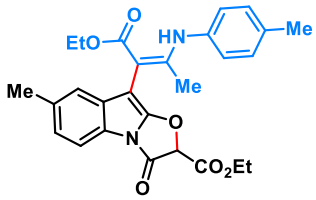
$C_{30}H_{26}BrN_2O_6$ $[M+H]^+$ 589.0969, found 589.0968.



Ethyl

6-bromo-9-(1-((4-bromophenyl)amino)-3-ethoxy-3-oxo-1-phenylprop-1-en-2-yl)-3-oxo-2,3-dihyd rooxazolo[3,2-*a*]indole-2-carboxylate (**5h**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 50:1 to 40:1); 82.6 mg, 62% yield; reaction time = 30 min; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.12 (s, 1H), 7.65 (d, J = 4.0 Hz, 1H), 7.33 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 1H), 7.14-7.06 (m, 5H), 6.66 (d, J = 8.0 Hz, 2H), 6.17-5.84 (m, 1H), 4.26 (q, J = 8.0 Hz, 2H), 4.20-4.10 (m, 2H), 1.24 (t, J = 8.0 Hz, 3H), 1.10 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.1, 162.8, 159.7, 159.4, 152.3, 139.2, 135.3, 133.7, 131.4, 129.1, 128.6, 127.9, 127.6, 124.7, 124.4, 121.3, 115.5, 114.7, 113.7, 88.5, 87.9, 84.3, 62.6, 59.6, 14.2, 13.9. IR (KBr) v 3431, 1766, 1652, 996, 773 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{25}Br_2N_2O_6$ $[M+H]^+$ 667.0074, found 667.0077.

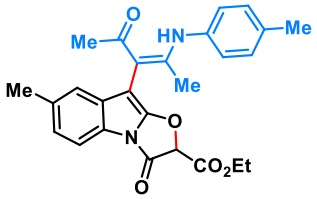


Ethyl

9-(1-ethoxy-1-oxo-3-(*p*-tolylamino)but-2-en-2-yl)-7-methyl-3-oxo-2,3-dihydrooxazolo[3,2-*a*]indo le-2-carboxylate (**5i**)

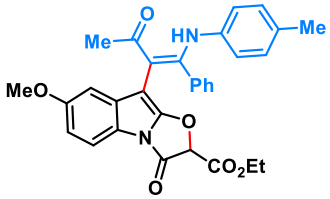
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 30:1 to 25:1); 73.1 mg, 77% yield; dr = 2:1 (determined by ^{13}C NMR, inseparable isomers); reaction time = 30 min; mp 67.5-68.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.07-7.01 (m, 4H), 5.56 (s, 1H), 4.41-4.32 (m, 2H), 4.26-4.02 (m, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 2.04 (s, 2H), 1.93 (s, 1H), 1.39-1.32 (m, 3H), 1.20-1.13 (m, 3H); ^{13}C NMR for the major isomer (100 MHz, $CDCl_3$) δ 170.0, 163.7, 160.8, 159.0, 151.8, 136.9, 136.6, 135.1, 134.8, 129.6, 125.1, 123.3, 120.6, 112.6, 89.9, 84.4, 84.3, 84.1, 63.1, 59.2, 21.8, 20.9, 17.8,

14.5, 14.0; ^{13}C NMR for the minor isomer (100 MHz, $CDCl_3$) δ 170.1, 163.3, 160.1, 159.0, 151.8, 136.9, 136.6, 135.1, 134.9, 129.6, 125.1, 123.5, 120.3, 112.7, 89.8, 84.4, 84.3, 84.1, 63.1, 59.3, 21.8, 20.9, 17.9, 14.4, 14.0. IR (KBr) *v* 3012, 1761, 1645, 1227, 1017 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_6$ $[M+H]^+$ 477.2026, found 477.2023.



Ethyl 7-methyl-3-oxo-9-(4-oxo-2-(*p*-tolylamino)pent-2-en-3-yl)-2,3-dihydrooxazolo[3,2-*a*]indole-2-carboxylate (**5j**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1 to 12:1); 48.9 mg, 55% yield; dr = 1.1:1 (determined by ^{13}C NMR, inseparable isomers); reaction time = 30 min; mp 77.4-78.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.68 (d, *J* = 28.0 Hz, 1H), 7.69 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.08-7.04 (m, 3H), 5.59 (d, *J* = 12.0 Hz, 1H), 4.39-4.31 (m, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.00 (q, *J* = 28.0 Hz, 6H), 1.36-1.32 (m, 3H); ^{13}C NMR for the major isomer (100 MHz, $CDCl_3$) δ 196.3, 163.5, 162.8, 162.2,159.0, 152.4, 136.7, 136.0, 135.7, 135.5, 129.6, 125.2, 123.8, 119.7, 112.9, 94.8, 91.2, 84.4, 63.2, 28.4, 21.7, 20.9, 17.5, 14.0; ^{13}C NMR for the minor isomer (100 MHz, $CDCl_3$) δ 196.9, 163.3, 162.8, 162.2, 159.1, 152.5, 136.6, 136.0, 135.8, 135.5, 129.7, 125.2, 123.6, 119.6, 112.9, 94.8, 91.1, 84.4, 63.3, 28.5, 21.7, 20.9, 17.7, 13.9. IR (KBr) *v* 3032, 2951, 1762, 1595, 1472, 1273, 1025 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{27}N_2O_5$ $[M+H]^+$ 447.1920, found 447.1929.

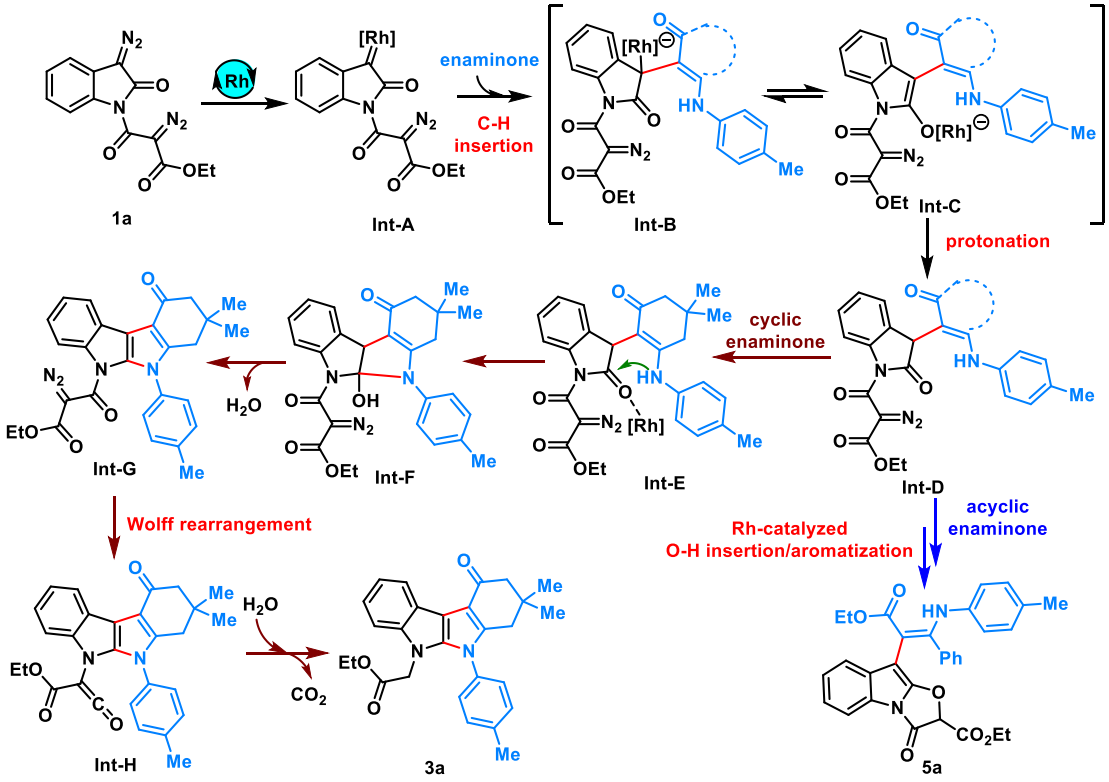


Ethyl 7-methoxy-3-oxo-9-(3-oxo-1-phenyl-1-(*p*-tolylamino)but-1-en-2-yl)-2,3-dihydrooxazolo[3,2-*a*]indole-2-carboxylate (**5k**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1 to 12:1); 55.6 mg, 71% yield; dr = 2:1 (determined by ^{1}H NMR, inseparable isomers); reaction time

= 30 min; mp 88.1-88.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.17 (d, *J* = 12.0 Hz, 1H), 7.57 (d, *J* = 12.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 12.0 Hz, 1H), 7.23-7.06 (m, 7H), 6.73-6.66 (m, 2H), 5.24 (s, 1H), 4.36-4.29 (m, 2H), 3.78 (d, *J* = 12.0 Hz, 1H), 2.37 (s, 3H), 2.05 (d, *J* = 27.0 Hz, 6H), 1.32 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR for the major isomer (75 MHz, $CDCl_3$) δ 193.3, 165.3, 163.4, 158.5, 157.9, 152.7, 142.5, 138.1, 136.1, 135.8, 129.8, 128.9, 127.2, 126.5, 125.2, 119.5, 113.8, 109.7, 103.9, 94.5, 92.3, 84.1, 63.2, 55.6, 20.9, 18.1, 14.0; ^{13}C NMR for the minor isomer (75 MHz, $CDCl_3$) δ 193.5, 164.7, 163.0, 158.7, 157.8, 152.7, 142.2, 138.0, 136.1, 135.8, 129.8, 128.9, 127.3, 126.8, 125.2, 119.4, 113.8, 109.8, 103.6, 94.3, 92.1, 84.3, 63.2, 55.6, 20.9, 18.1, 14.0. IR (KBr) *v* 2986, 1761, 1578, 1477, 1284, 1056 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{29}N_2O_6$ $[M+H]^+$ 525.2026, found 525.2030.

5. Mechanistic studies

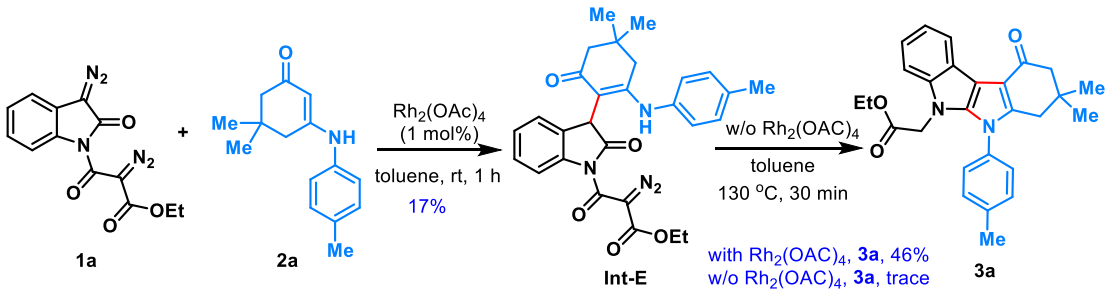


Scheme S1 Proposed mechanism

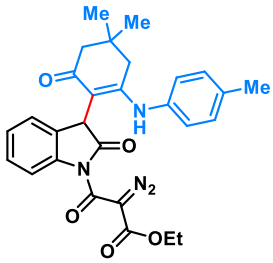
On the basis of the experimental results and previous reports on bis(diazo)indolin-2-one chemistry, we proposed a possible mechanism to rationalize the reaction pathway for the formation of **3a** and **5a**. As shown in Scheme S1, this reaction began with the Rh(II)-catalyzed decomposition of bis(diazo)indolin-2-one **1a** into metallocarbenoid **Int-A**. The **Int-A** was highly reactive and could be intercepted by enaminone **2a** or **4a** to generate **Int-B**, which was in

equilibrium with **Int-C**. Followed by protonation, **Int-D** was afforded. Then, two distinct pathways were involved. For cyclic enaminone **2a**, the rigid nature of **2a** compelled the amino group to attack the carbonyl group of the oxindole ring to produce **Int-F**, which easily underwent dehydration to generate aromatized intermediate **Int-G**. Followed by Wolff rearrangement and subsequent hydrolysis, the desired **3a** was afforded in the end, with the release of one equivalent of CO_2. While for acyclic enaminone **4a**, it was comparably more flexible and could form an intramolecular H-bonding between the N-H and the carbonyl group of the ester moiety. As such, a Rh(II)-catalyzed O-H insertion and aromatization sequence took place from **Int-D** to produce **5a**.

To get some evidence, a control experiment was conducted (Scheme S2). We attempted the model reaction of **1a** and **2a** at room temperature. After 1h, the **Int-E** was obtained in 17% yield without the formation of any **3a**. By subjecting **Int-E** to refluxing toluene, the reaction went very sluggishly and we could only detect the formation of trace amount of **3a**. However, addition of $Rh_2(OAc)_4$ (1 mol%) was beneficial to this transformation and it went completion within 30 min to afford **3a** in 46% yield. This implied that **Int-E** was likely one of the key intermediates and $Rh_2(OAc)_4$ was crucial for subsequent conversion.



Scheme S2 Control experiment



Ethyl

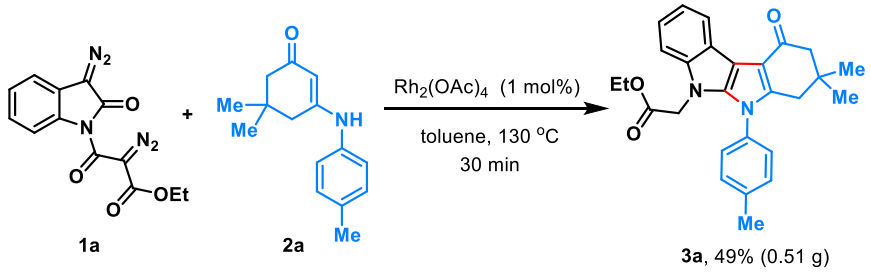
2-diazo-3-(3-(4,4-dimethyl-6-oxo-2-(*p*-tolylamino)cyclohex-1-en-1-yl)-2-oxoindolin-1-yl)-3-oxop ropanoate (**Int-E**)

The preparation of **Int-E** was performed on a 0.2 mmol scale at room temperature. Brown solid

obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 17.4 mg, 17% yield; reaction time = 1 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 3H), 7.10 (t, *J* = 8.0 Hz, 3H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.87 (s, 1H), 4.31 (q, *J* = 8.0 Hz, 2H), 2.39-2.36 (m, 7H), 1.31 (t, *J* = 8.0 Hz, 3H), 1.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 177.1, 163.7, 161.3, 159.3, 139.0, 136.3, 130.4, 130.2, 128.4, 128.0, 127.0, 126.8, 126.8, 125.8, 125.6, 115.8, 61.6, 50.8, 45.8, 37.1, 34.3, 28.9, 28.4, 21.1, 14.3. IR (KBr) *v* 3284, 2963, 2141, 1700, 1653, 1517, 1395, 1319, 1114, 757 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{29}N_4O_5$ $[M+H]^+$ 501.2132, found 501.2129.

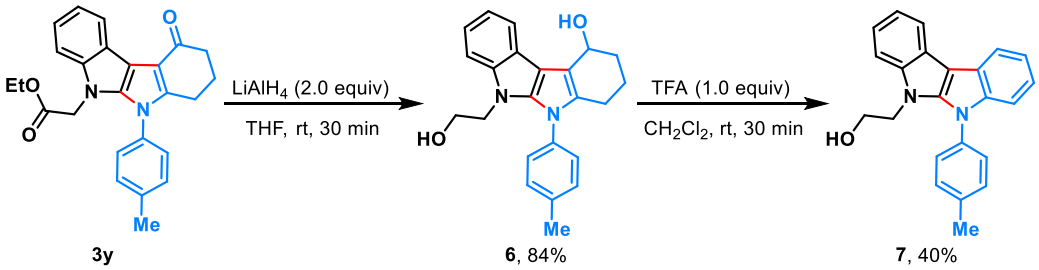
6. Methodology application

6.1 Scalable preparation of 3a



General procedure for scalable preparation of 3: To a solution of bis(diazo)indolin-2-one **1a** (0.72 g, 2.4 mmol) and enaminone **2a** (0.55 g, 2.4 mmol) in toluene (12 mL) was added $Rh_2(OAc)_4$ (10.6 mg, 0.024 mmol). After being stirred at 130 °C for 30 min, the mixture was concentrated in vacuum. The residue was purified via flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 8:1 to 6:1) to afford the corresponding product **3a** as light yellow solid in 49% yield (0.51 g).

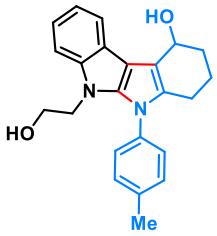
6.2 Chemical conversions of 3y



General procedure for the formation of 6: Under nitrogen atmosphere, to a solution of **3y** (160.2 mg, 0.40 mmol) in dry THF (2.0 mL) was added $LiAlH_4$ by syringe (2.4 M in hexane, 0.32 mL) successively. The resulting reaction mixture was stirred at room temperature for 30 min. Then,

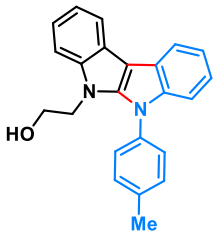
saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2 for three times. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **6** in 84% yield (121.6 mg). (*Note: product **6** was not stable in air.*)

General procedure for the formation of 7: To a solution of **6** (36.0 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was TFA (7.4 μL, 0.10 mmol). The resulting reaction mixture was stirred at room temperature for 30 min. Then, the mixture was concentrated in vacuum. The residue was purified via flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1) to afford the corresponding product **7** as white solid in 40% yield (13.5 mg).



6-(2-Hydroxyethyl)-5-(*p*-tolyl)-1,2,3,4,5,6-hexahydroindolo[2,3-*b*]indol-1-ol (**6**)

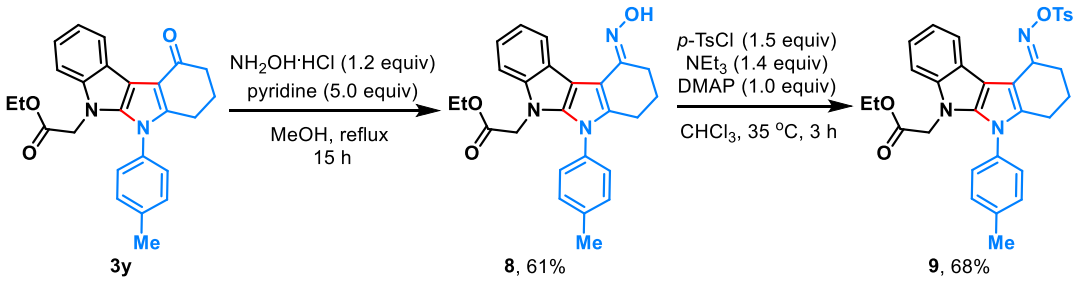
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 121.6 mg, 84% yield; reaction time = 30 min; mp 158.9-159.7 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 7.69-7.66 (m, 1H), 7.38-7.32 (m, 5H), 7.04-6.98 (m, 2H), 4.89 (s, 2H), 4.64 (s, 1H), 3.88 (t, *J* = 8.0 Hz, 2H), 3.27 (s, 2H), 2.41 (s, 3H), 2.31 (d, *J* = 16.0 Hz, 2H), 1.95 (d, *J* = 12.0 Hz, 2H), 1.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 139.4, 138.7, 137.7, 134.2, 130.0, 128.7, 127.6, 121.0, 119.0, 118.8, 118.4, 114.0, 109.7, 105.7, 63.6, 59.2, 45.4, 33.5, 22.4, 20.8, 19.8. IR (KBr) *v* 3046, 2937, 1521, 1057, 742 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{24}N_2NaO_2$ $[M+Na]^+$ 383.1730, found 383.1727.



2-(6-(*p*-Tolyl)indolo[2,3-*b*]indol-5(6*H*)-yl)ethan-1-ol (**7**)

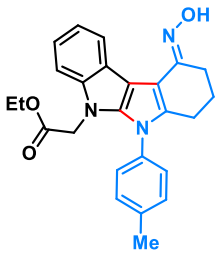
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 13.5 mg, 40% yield; reaction time = 30 min; mp 168.7-169.4 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 8.0 Hz, 2H), 7.44-7.37 (m, 5H), 7.30 (d, *J* = 12.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.16-7.10 (m,

2H), 4.10 (t, *J* = 8.0 Hz, 2H), 3.64 (t, *J* = 8.0 Hz, 2H), 2.51 (s, 3H), 1.46-1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.6, 139.6, 139.0, 134.2, 130.4, 128.3, 122.0, 121.9, 120.8, 120.4, 120.0, 119.9, 118.5, 118.1, 110.3, 109.7, 101.3, 61.4, 45.7, 21.3. IR (KBr) *v* 3512, 3043, 1523, 1455, 745 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{20}N_2NaO$ $[M+Na]^+$ 363.1468, found 363.1470.



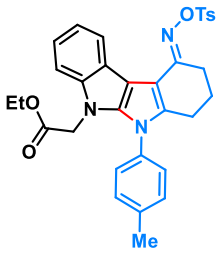
General procedure for the formation of 8: To a solution of **3y** (80.1 mg, 0.20 mmol) in MeOH (5.0 mL) was hydroxylamine hydrochloride (16.7 mg, 0.24 mmol) and pyridine (80.6 μL, 1.0 mmol). The resulting reaction mixture was stirred at 65 °C for 15 h. Then, the mixture was concentrated in vacuum. The residue was purified via flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 8:1) to afford the corresponding product **8** as white solid in 61% yield (50.8 mg).

General procedure for the formation of 9： To a solution of **8** (41.5 mg, 0.10 mmol) in 1.0 mL of DCM, *p*-TsCl (28.6 mg, 015 mmol), DMAP (12.2 mg, 0.10 mmol) and Et_3N (19.5 μL, 0.14 mmol) were successively added. The resulting mixture was stirred at 35 °C for 3 h, then diluted with Et_2O, washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, concentrated and purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1) to afford **9** as a light yellow solid in 68% yield.



Ethyl 2-(10-(hydroxyimino)-6-(*p*-tolyl)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**8**)
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1); 50.8 mg, 61% yield; reaction time = 15 h; mp 167.3-168.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.17 (m, 1H), 7.28 (m, 4H), 7.20-7.10 (m, 3H), 7.02 (br, 1H), 4.48 (s, 2H), 4.05 (q, *J* = 8.0 Hz, 2H), 2.87 (t,

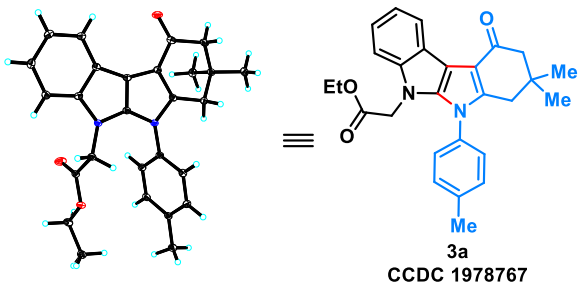
J = 8.0 Hz, 2H), 2.54 (t, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 2.06-1.96 (m, 2H), 1.14 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 154.5, 140.0, 139.2, 138.9, 135.6, 133.7, 130.1, 127.7, 121.8, 120.9, 120.4, 119.9, 108.3, 108.2, 103.8, 61.3, 45.2, 22.5, 22.4, 22.3, 21.2, 14.1. IR (KBr) *v* 3406, 2927, 1739, 1525, 1208, 740 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{26}N_3O_3$ $[M+H]^+$ 416.1969, found 416.1968.



Ethyl 2-(6-(*p*-tolyl)-10-((tosyloxy)imino)-7,8,9,10-tetrahydroindolo[2,3-*b*]indol-5(6*H*)-yl)acetate (**9**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 38.6 mg, 68% yield; reaction time = 3 h; mp 230.2-231.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.09-7.04 (m, 2H), 4.42 (s, 2H), 4.02 (q, *J* = 8.0 Hz, 2H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.51 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 2.01-1.95 (m, 2H), 1.13 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 161.8, 144.4, 139.8, 139.4, 139.1, 138.9, 133.4, 133.0, 130.2, 129.5, 128.9, 127.5, 121.3, 121.2, 120.8, 119.9, 108.2, 105.4, 103.5, 61.4, 45.0, 24.3, 22.2, 22.0, 21.7, 21.2, 14.0. IR (KBr) *v* 3442, 2927, 1638, 1180, 738 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{32}N_3O_5S$ $[M+H]^+$ 570.2057, found 570.2054.

7. Crystal structures of 3a and 7

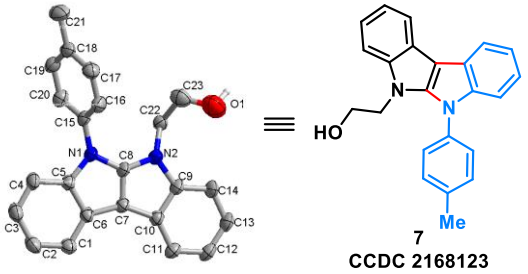


Displacement ellipsoids are drawn at the 30% probability level.

Table S1. Crystal data and structure refinement for **3a**.

Identification code global

Empirical formula	$C_{27}H_{28}N_2O_3$
Formula weight	428.51
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 11.0515(3) Å = 90°.
	b = 21.2790(6) Å = 100.6080(10)°.
	c = 9.5549(3) Å = 90°.
Volume	2208.58(11) $Å^3$
Z	4
Density (calculated)	1.289 Mg/m^3
Absorption coefficient	0.671 mm^{-1}
F(000)	912
Crystal size	0.430 x 0.350 x 0.160 mm^3
Theta range for data collection	4.07 to 72.37°.
Index ranges	-12<=h<=13, -26<=k<=26, -11<=l<=9
Reflections collected	22635
Independent reflections	4355 [R(int) = 0.0453]
Completeness to theta = 72.37°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.90 and 0.71
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4355 / 0 / 293
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.1000
R indices (all data)	R1 = 0.0424, wR2 = 0.1025
Largest diff. peak and hole	0.270 and -0.266 $e.Å^{-3}$



Displacement ellipsoids are drawn at the 30% probability level.

Table S2. Crystal data and structure refinement for **7**.

Bond precision: C-C = 0.0040 A Wavelength=0.71073

Cell: a = 9.674(3) b = 9.935(3) c = 10.704(3)

alpha = 87.411(11) beta = 65.196(11) gamma = 76.494(12)

Temperature: 273 K

	Calculated	Reported
Volume	906.4(5)	906.5(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{23}H_{20}N_2O$	$C_{23}H_{20}N_2O$
Sum formula	$C_{23}H_{20}N_2O$	$C_{23}H_{20}N_2O$
Mr	340.41	340.41
Dx,g cm-3	1.247	1.247
Z	2	2
Mu (mm-1)	0.077	0.077
F000	360.0	360.0
F000'	360.14	
h,k,lmax	12,12,13	12,12,13
Nref	3701	3682
Tmin,Tmax	0.983,0.988	0.521,0.746
Tmin'	0.979	

Correction method= # Reported T Limits: Tmin=0.521 Tmax=0.746 AbsCorr =

MULTI-SCAN

Data completeness= 0.995 Theta(max)= 26.358

R(reflections)= 0.0814(2493) wR2(reflections)= 0.2680(3682)

S = 1.068 Npar= 248

8. References

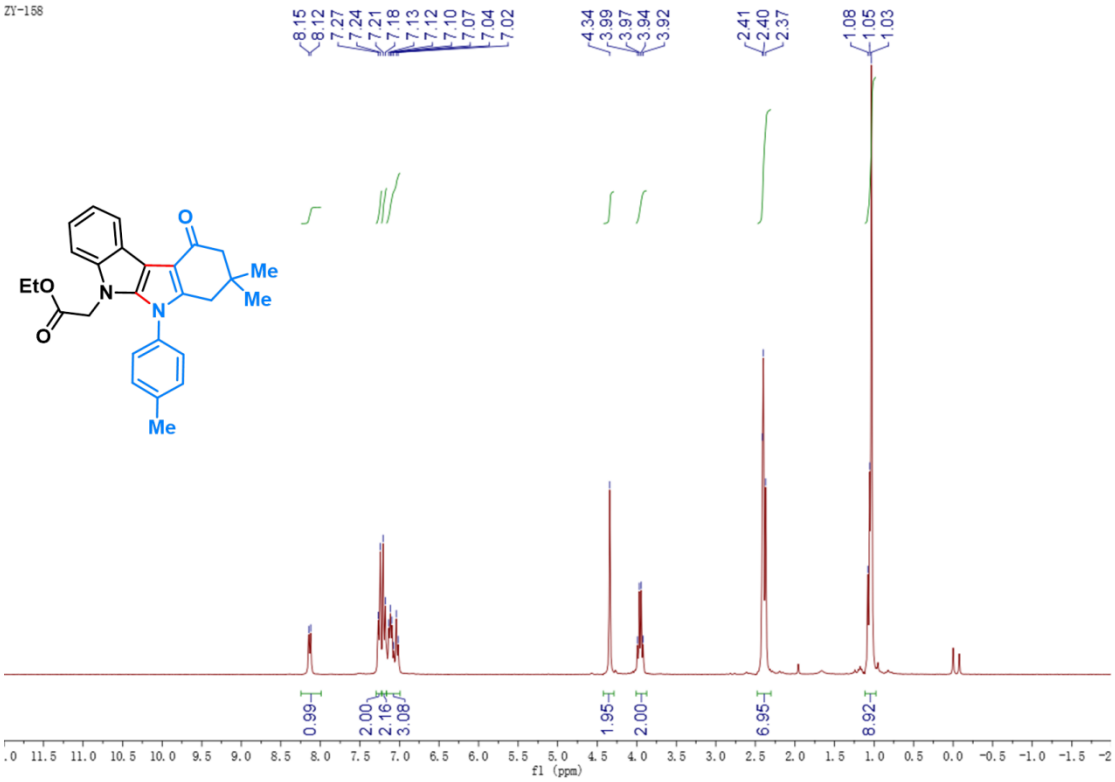
[1] (a) S. A. Bonderoff and A. Padwa, *J. Org. Chem.*, 2017, **82**, 642-651; (b) H. Li, S. A. Bonderoff, B. Cheng and A. Padwa, *J. Org. Chem.*, 2014, **79**, 392-400; (c) S. A. Bonderoff and A. Padwa, *Org. Lett.*, 2013, **15**, 4114-4117.

[2] D. Bhattacherjee, V. Thakur, S. Sharma, S. Kumar, R. Bharti, C. B. Reddy and P. Das, *Adv. Synth. Catal.*, 2017, **359**, 2209-2214.

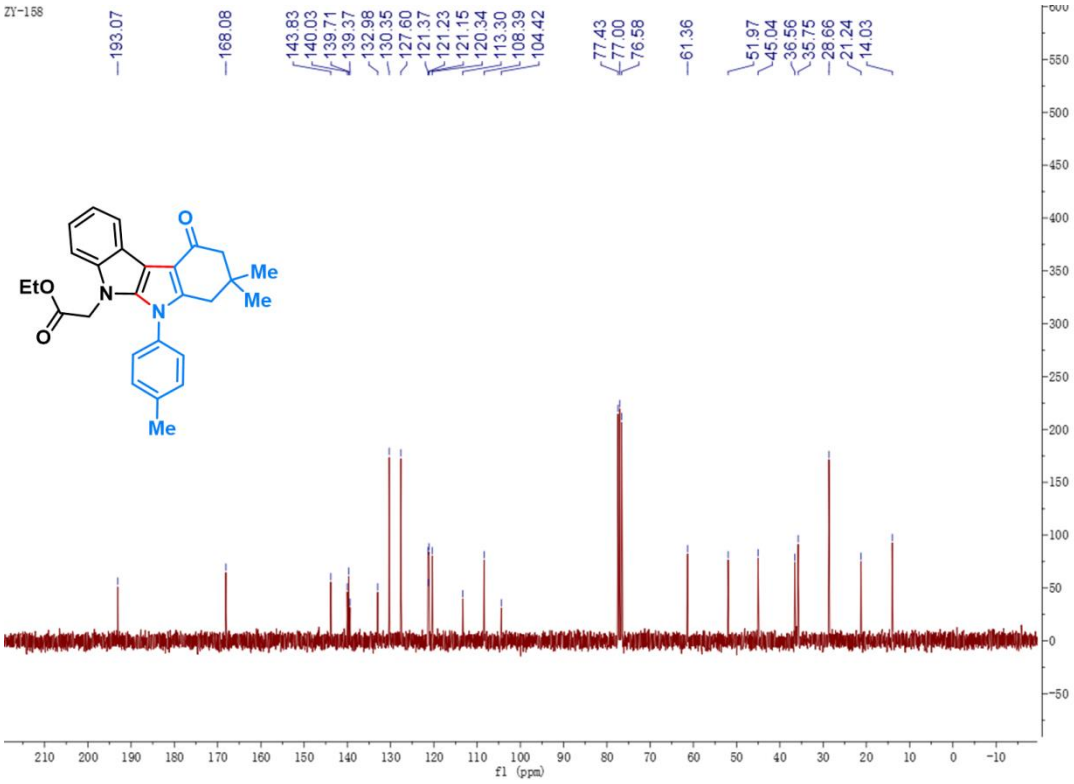
[3] (a) W.-Z. Qiao, T.-Q. Song, P. Cheng and B. Zhao, *Angew. Chem. Int. Ed.*, 2019, **58**, 13302-13307; (b) M.-X. Dong, X.-Y. Gao, Y. Xiang, L.-F. Li, S.-N. Li, X.-X. Wang, Z.-Q. Li and H.-J. Zhu, *Tetrahedron*, 2021, **82**, 131924; (c) W.-B. Liu, C. Chen and Q. Zhang, *J. Chem. Res.*, 2012, **36**, 175-177; (d) Z.-W. Chen, G. Shi, W. Tang, J. Sun and W.-X. Wang, *Eur. J. Org. Chem.*, 2021, 951-955.

9. NMR spectra

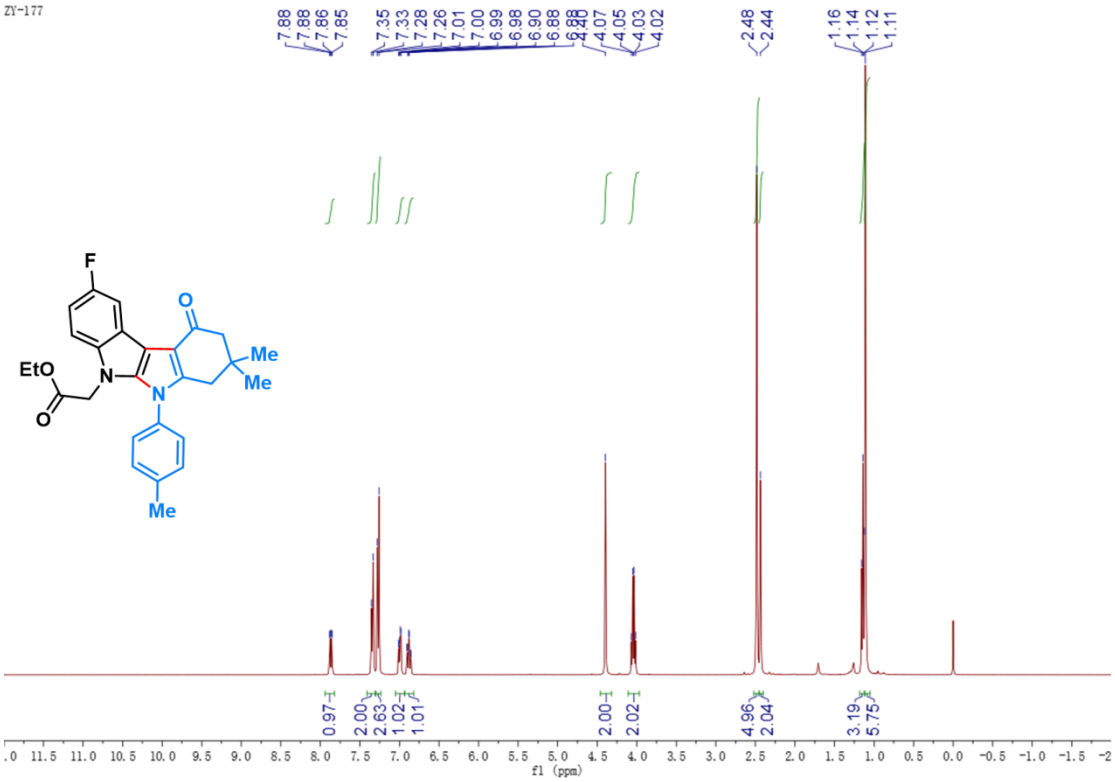
^{1}H NMR spectra of **3a**



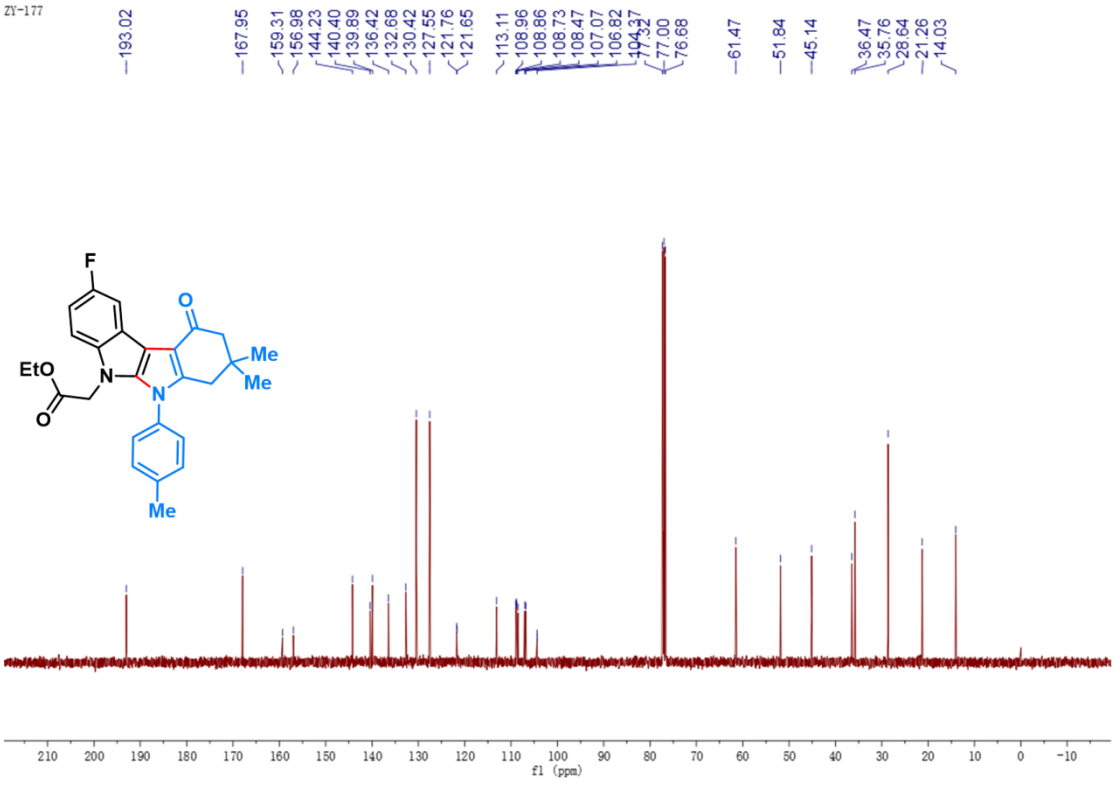
^{13}C NMR spectra of **3a**



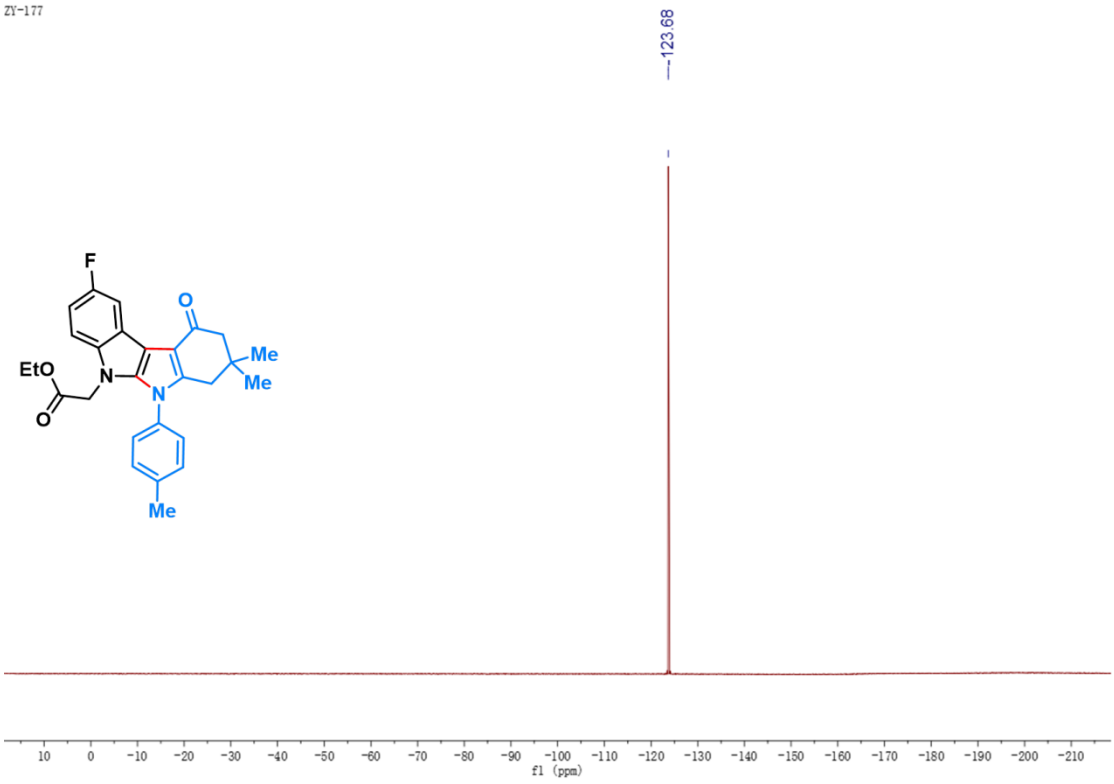
^{1}H NMR spectra of **3b**



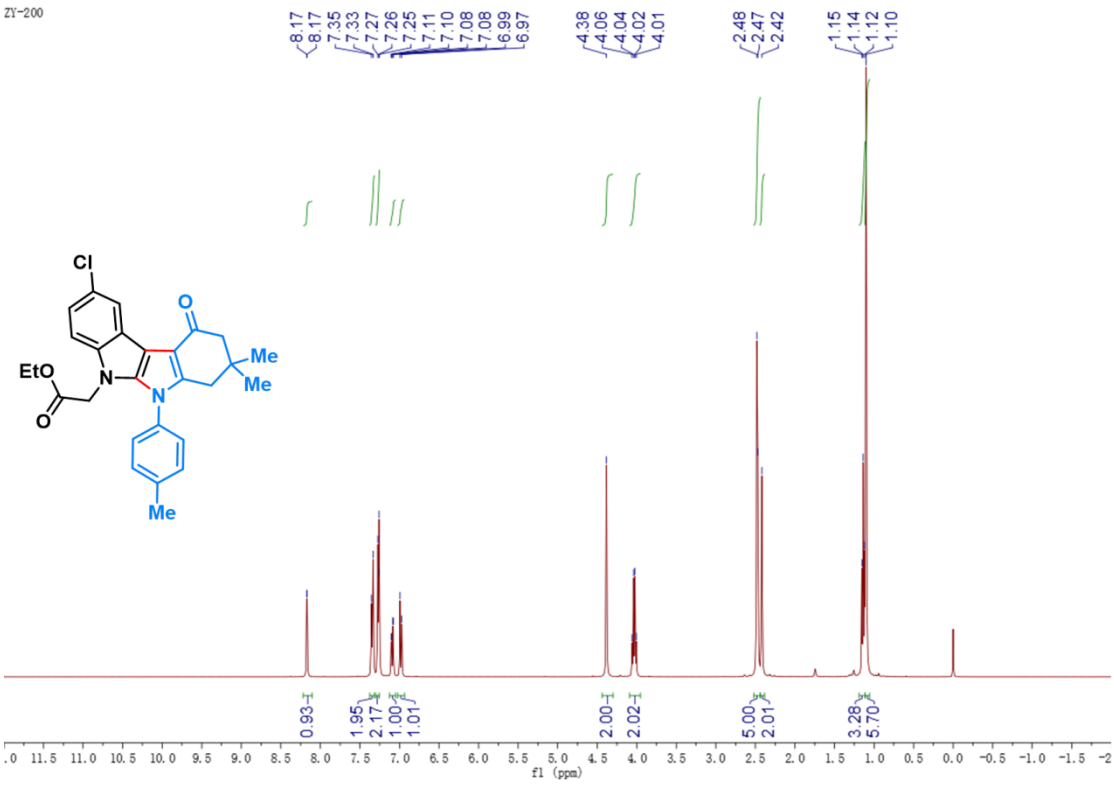
^{13}C NMR spectra of **3b**



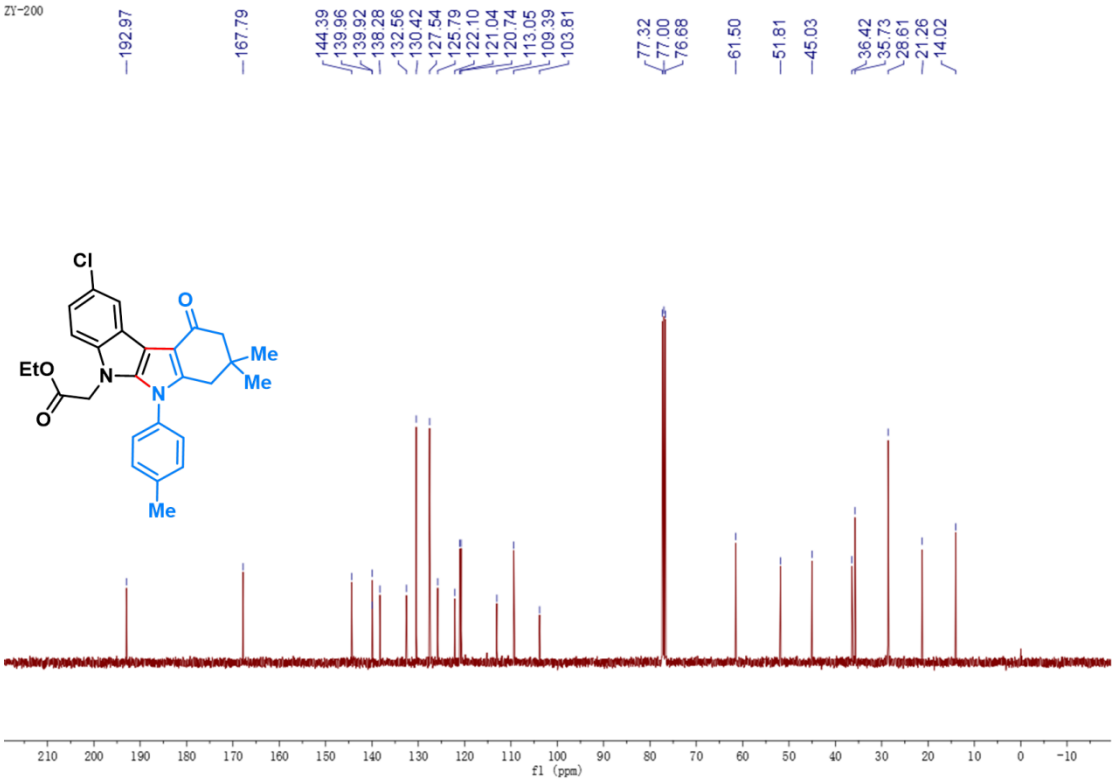
^{19}F NMR spectra of **3b**



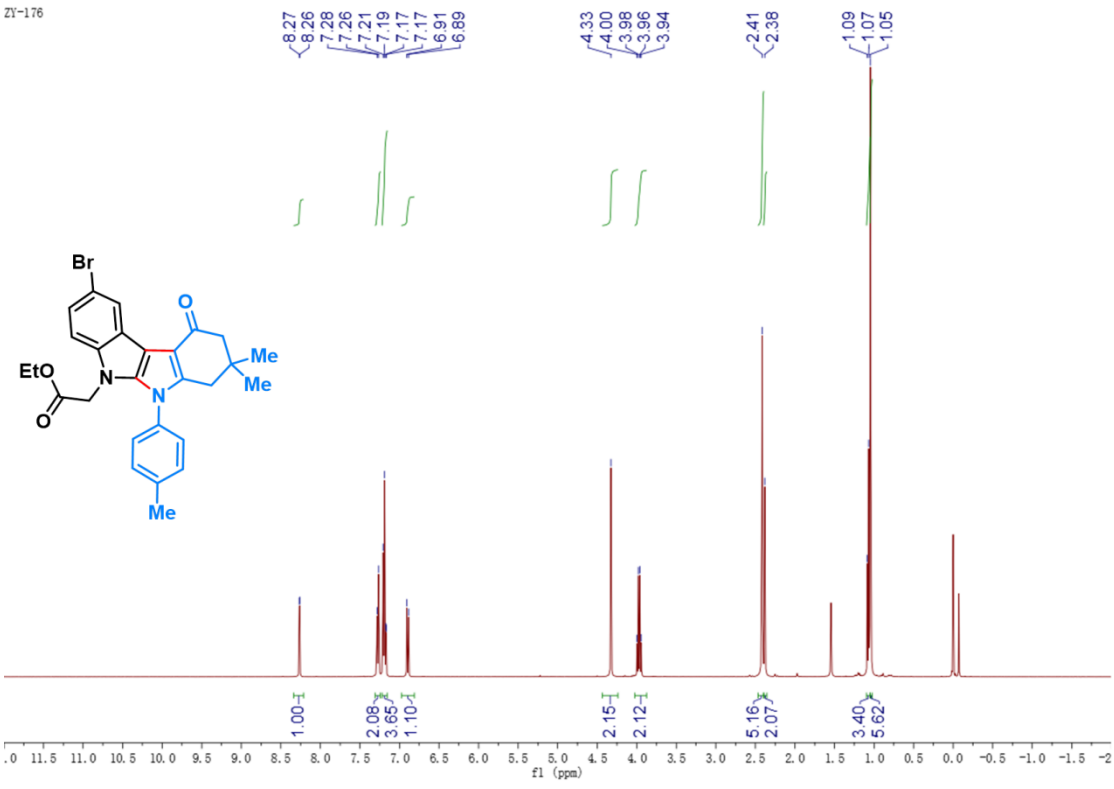
^{1}H NMR spectra of **3c**



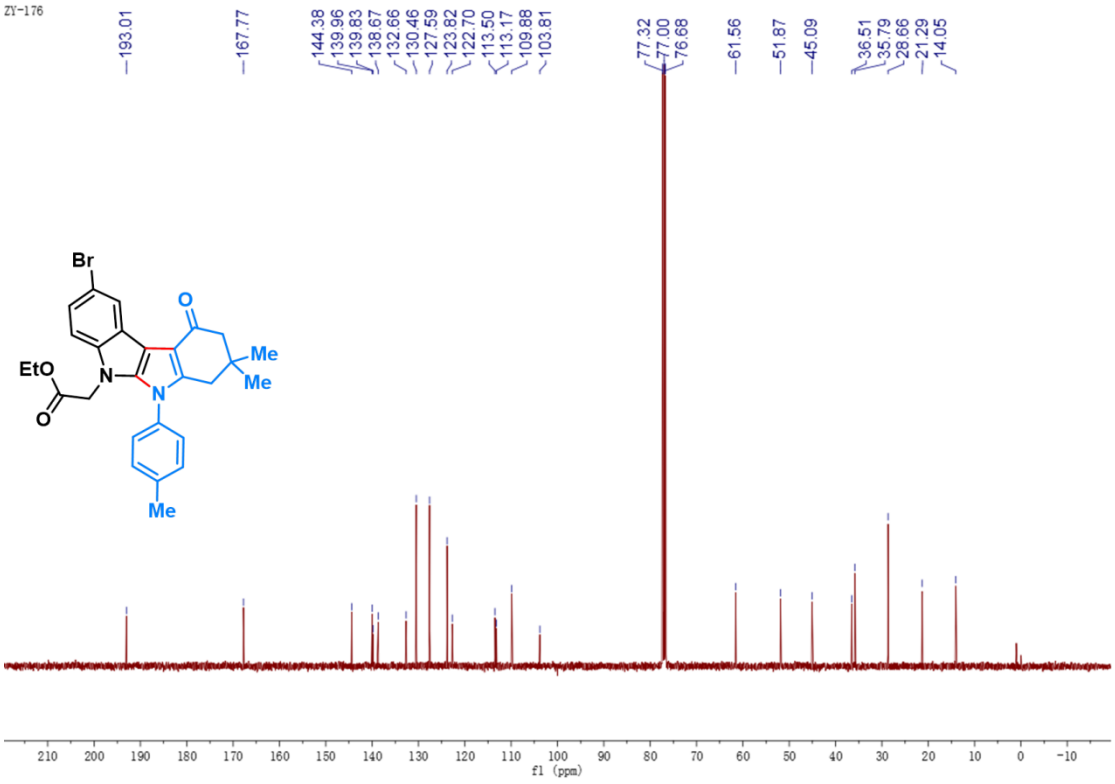
^{13}C NMR spectra of **3c**



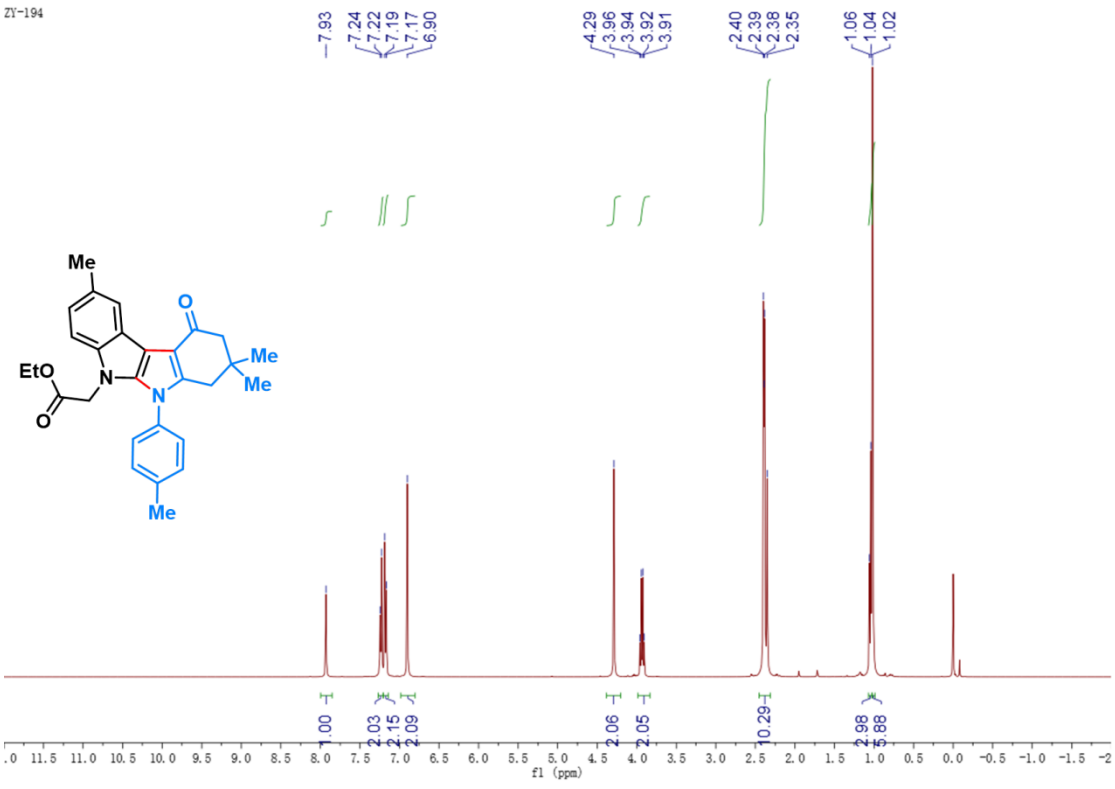
^{1}H NMR spectra of **3d**



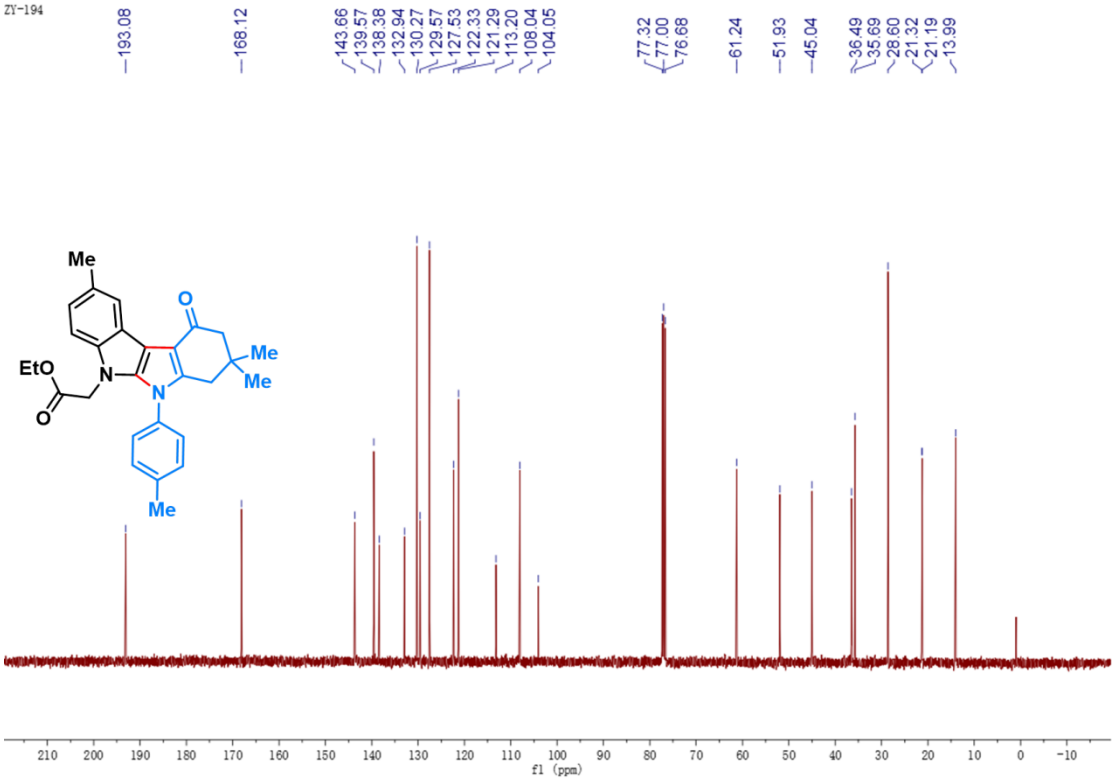
^{13}C NMR spectra of **3d**



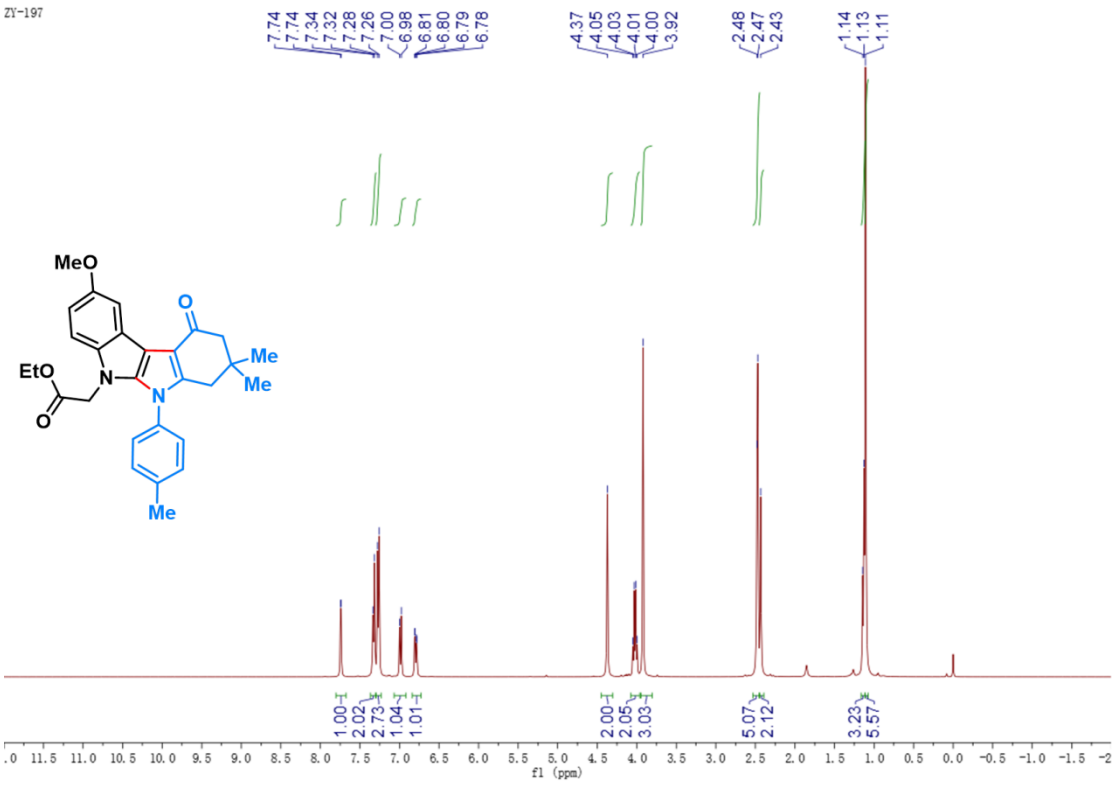
^{1}H NMR spectra of **3e**



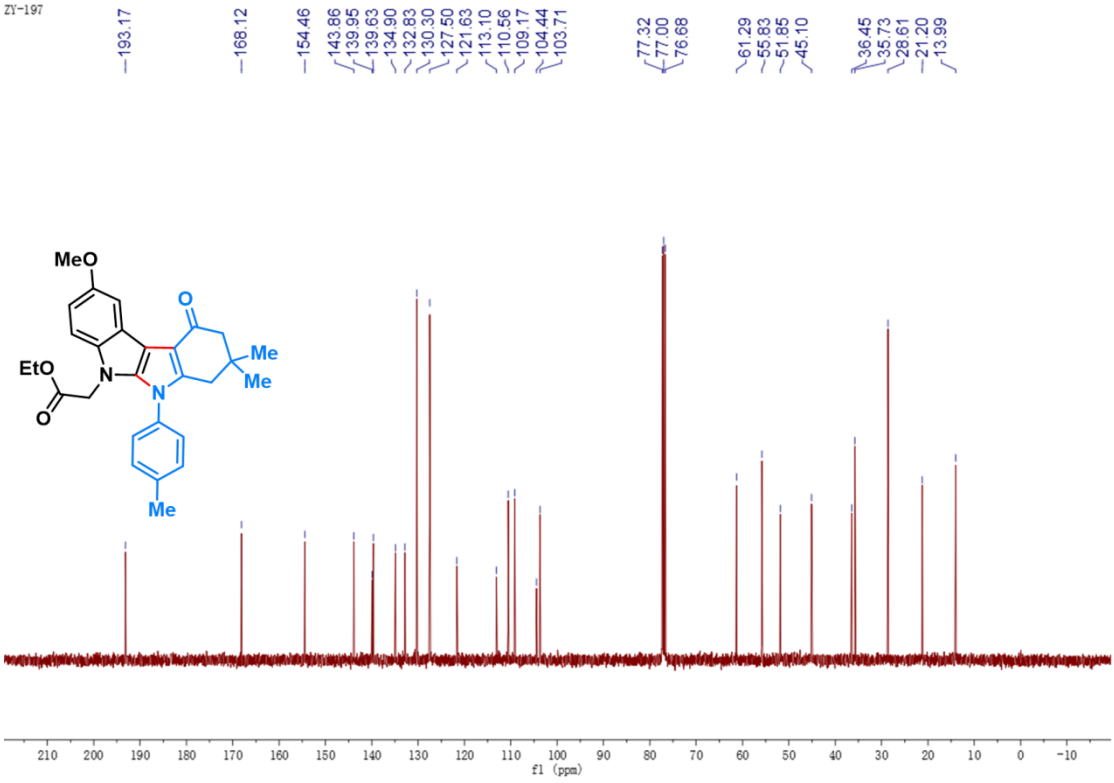
^{13}C NMR spectra of **3e**



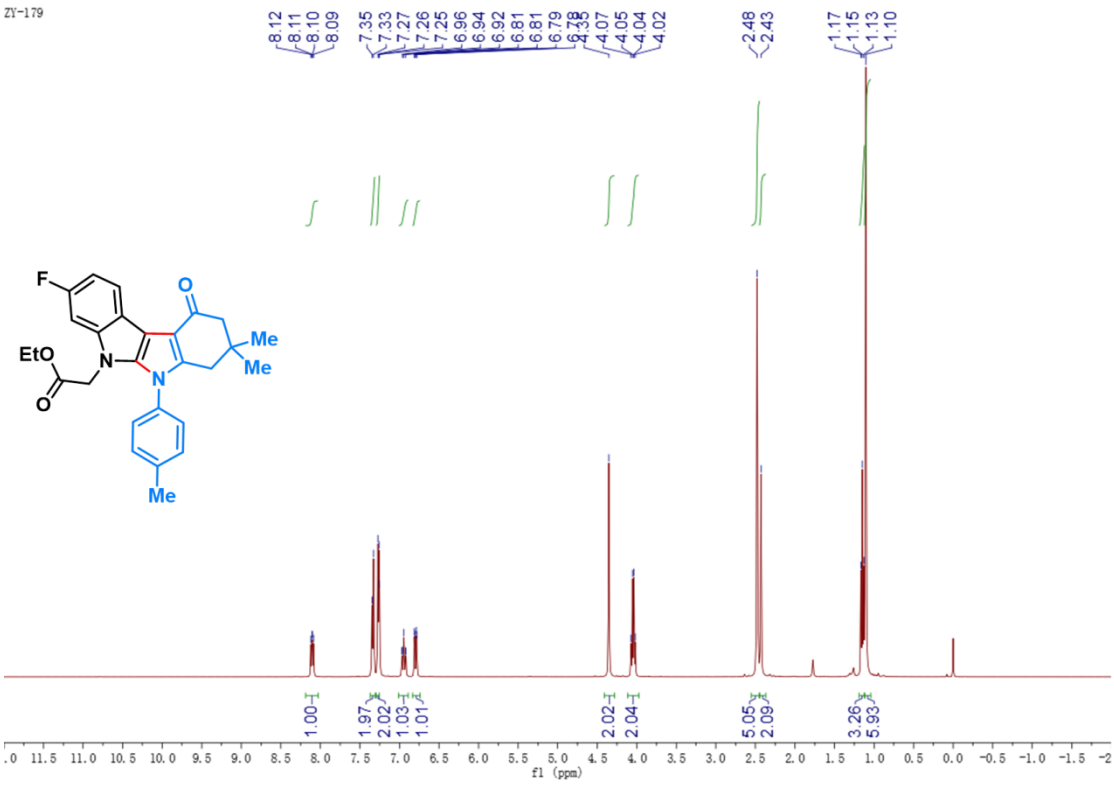
^{1}H NMR spectra of **3f**



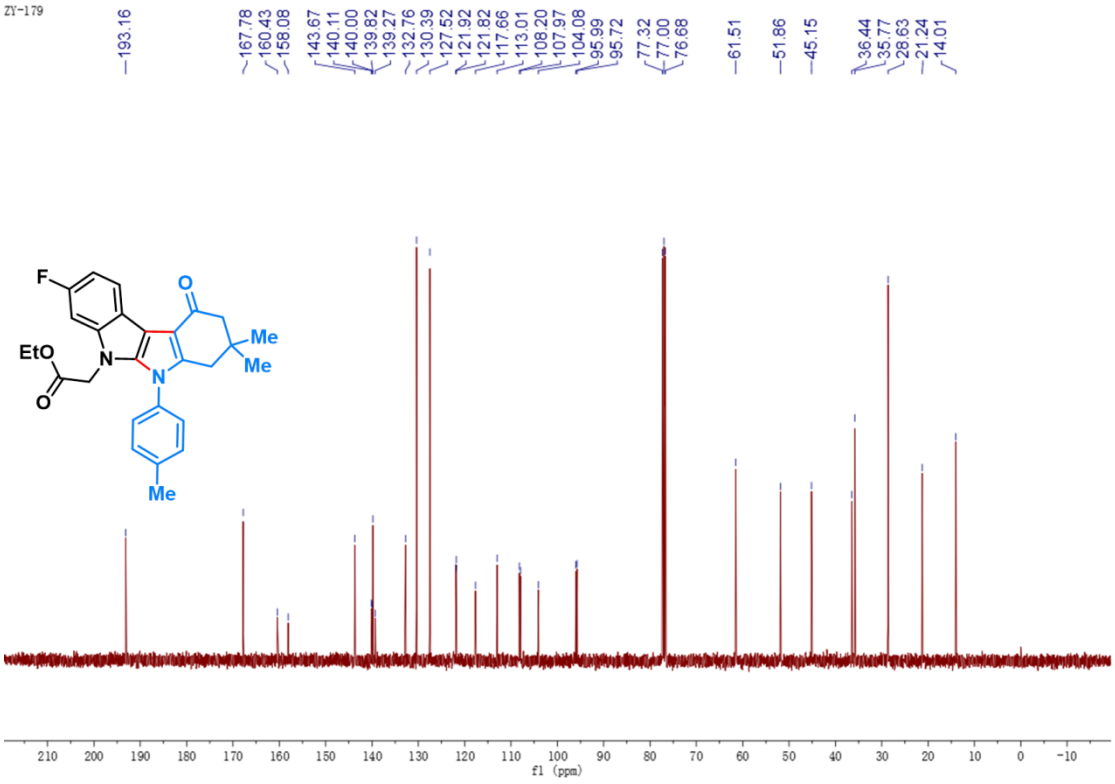
^{13}C NMR spectra of **3f**



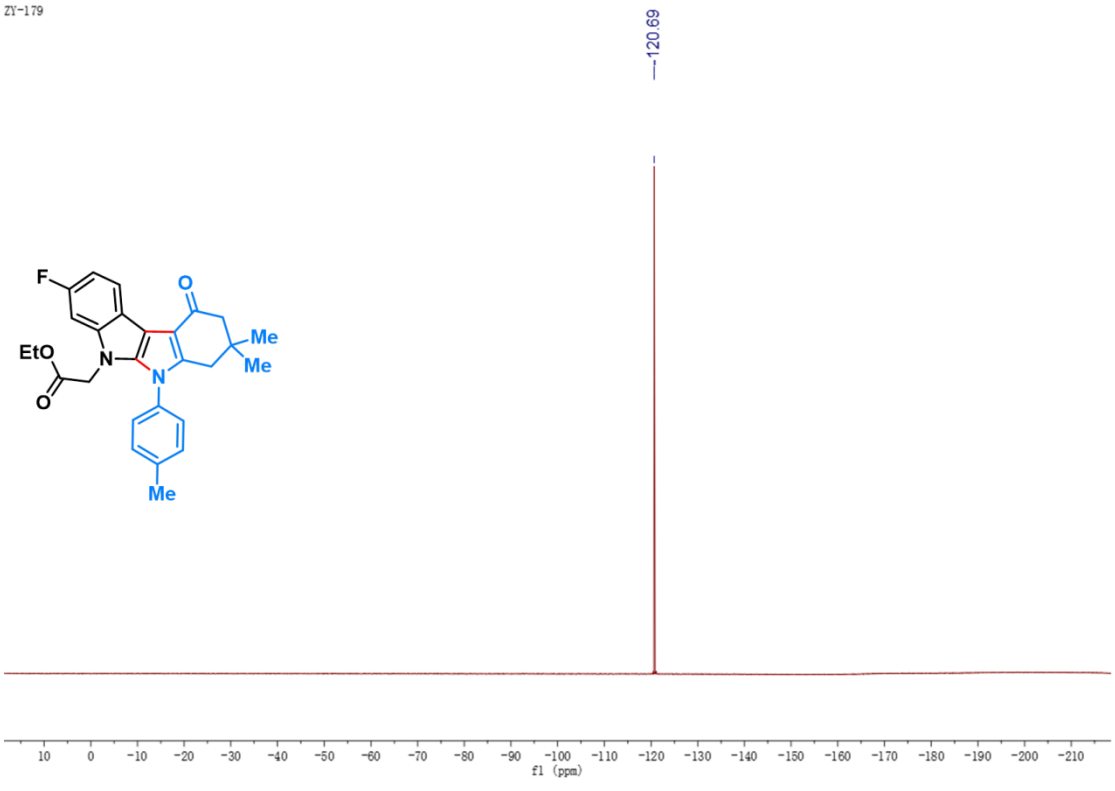
^{1}H NMR spectra of **3g**



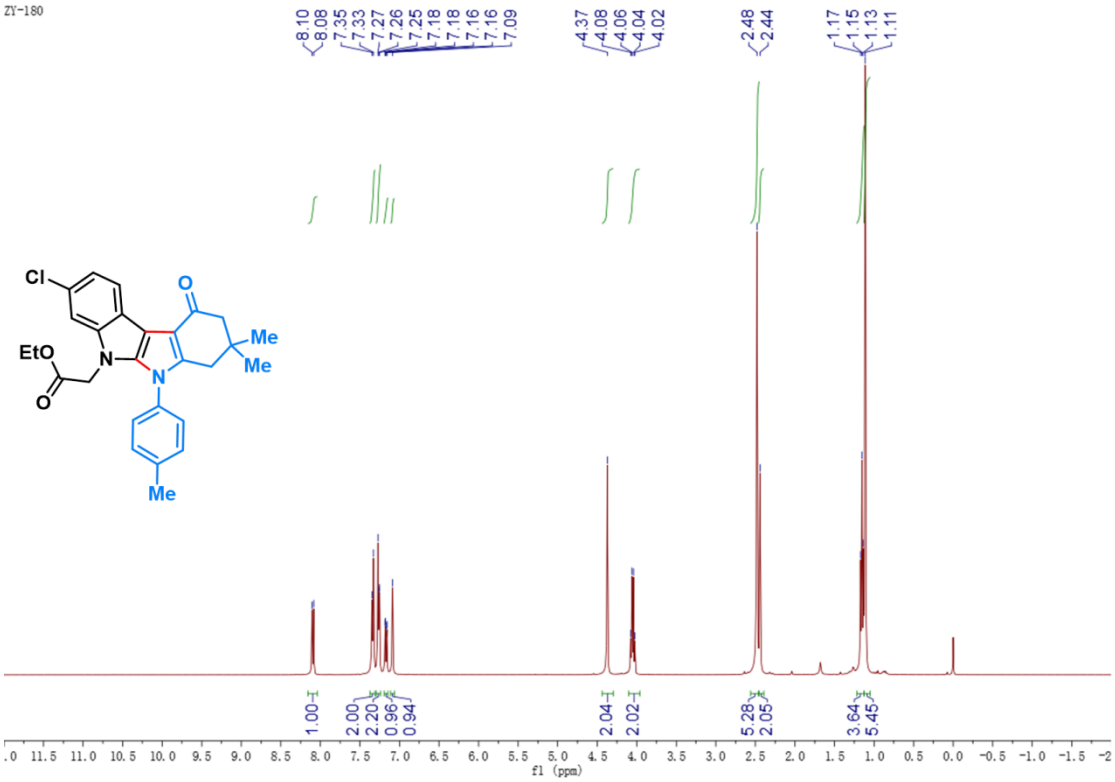
^{13}C NMR spectra of **3g**



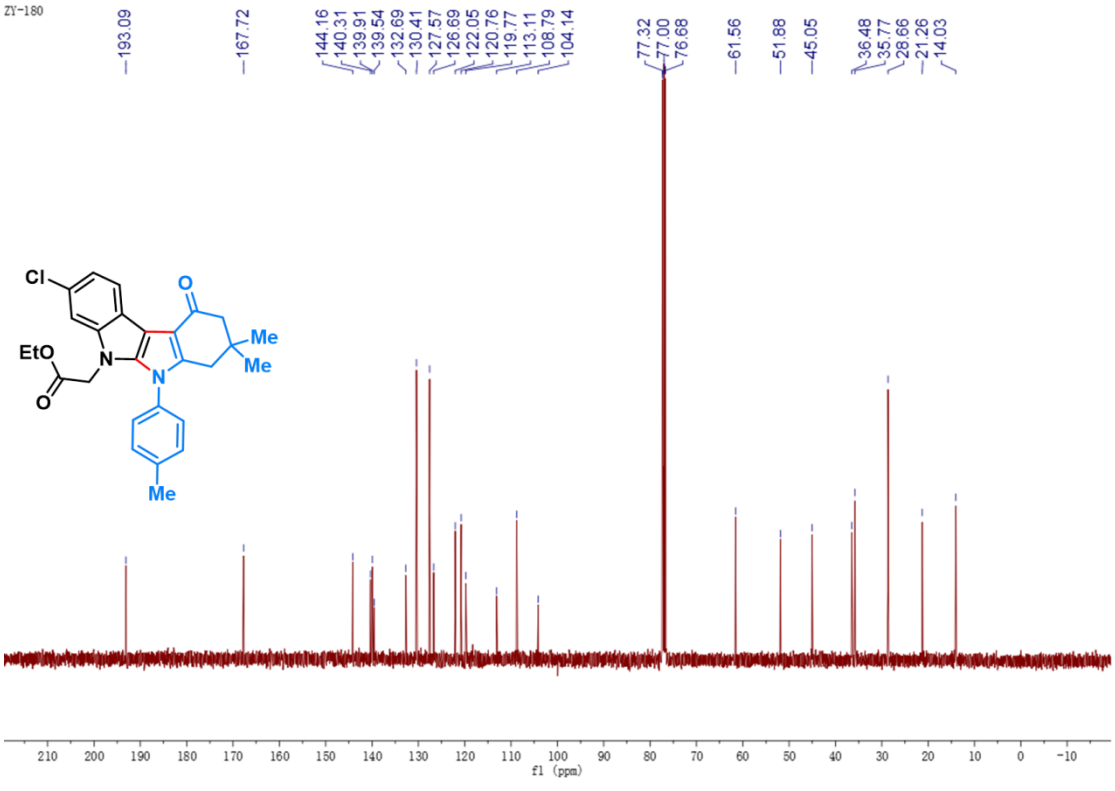
^{19}F NMR spectra of **3g**



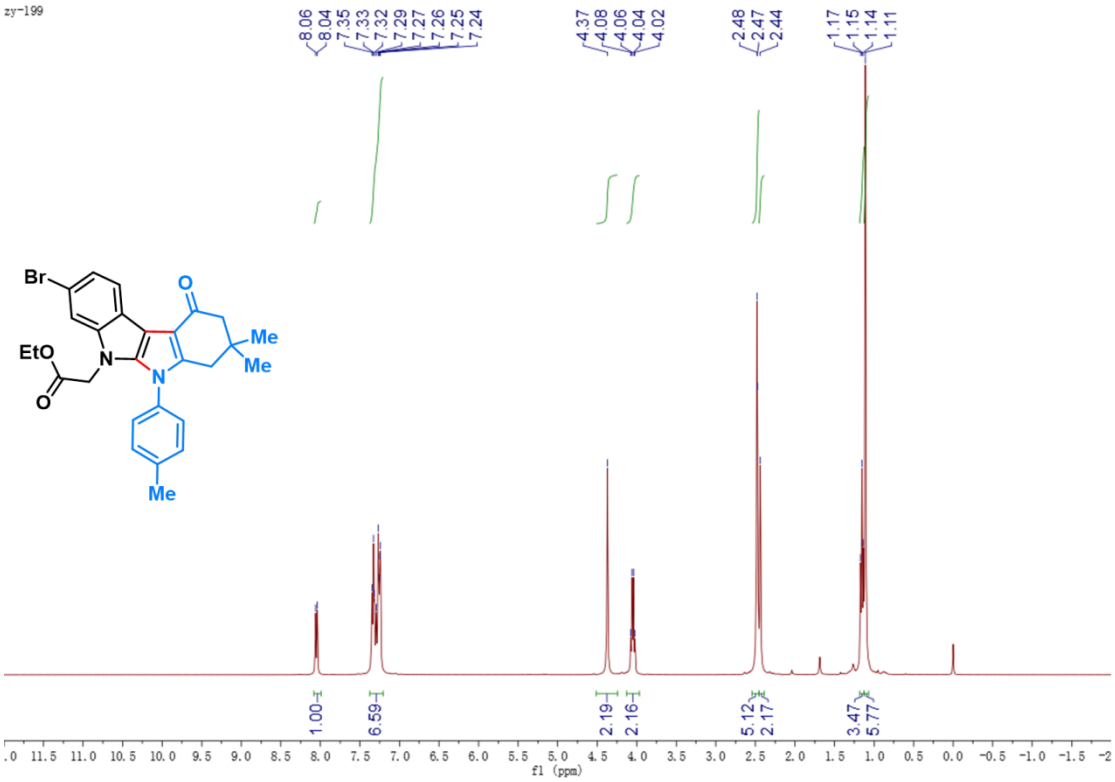
^{1}H NMR spectra of **3h**



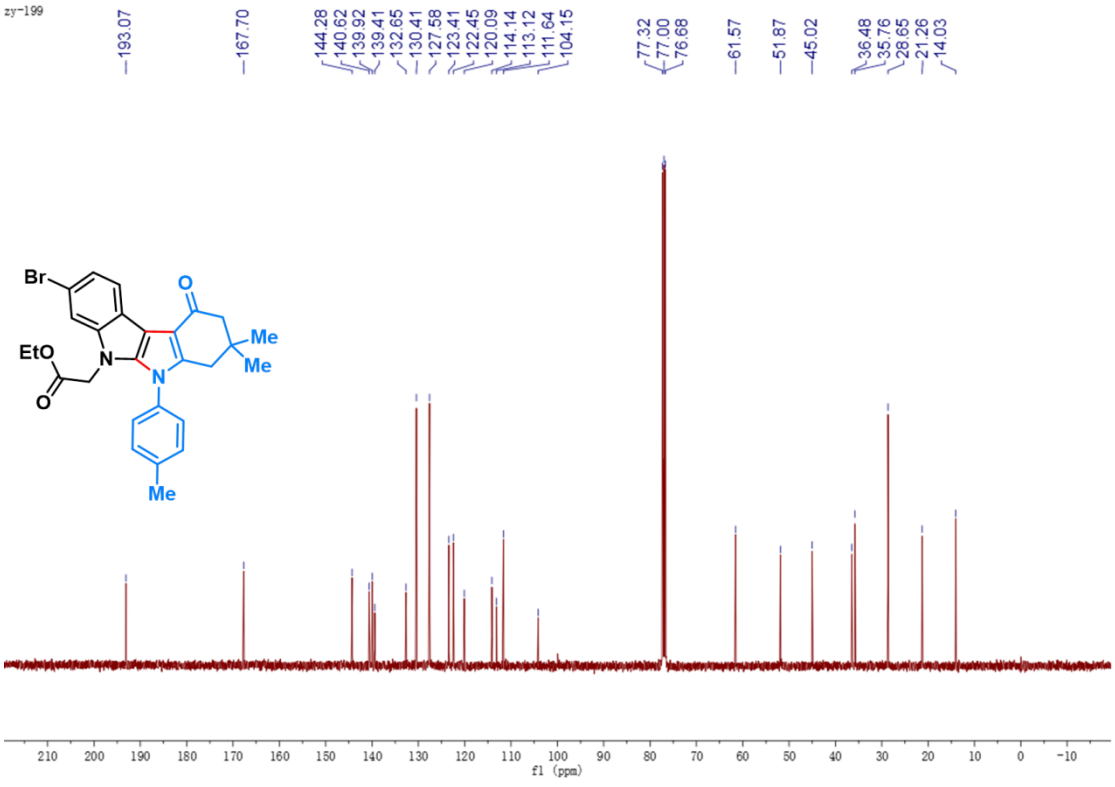
^{13}C NMR spectra of **3h**



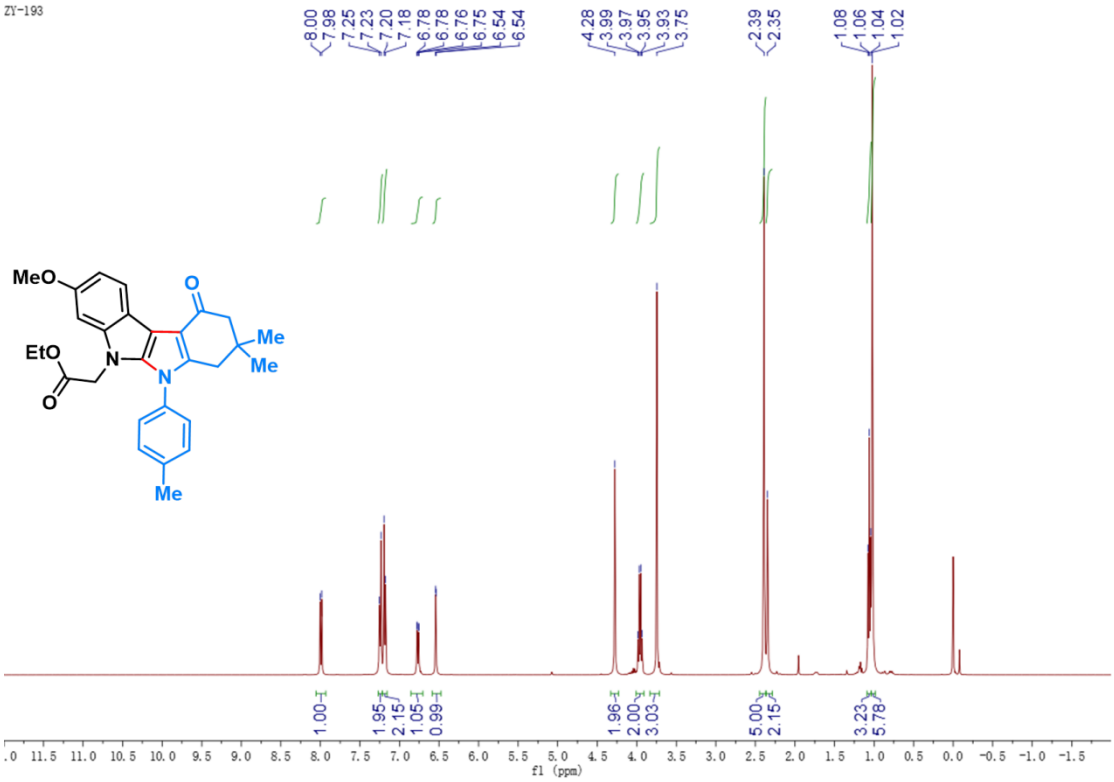
^{1}H NMR spectra of **3i**



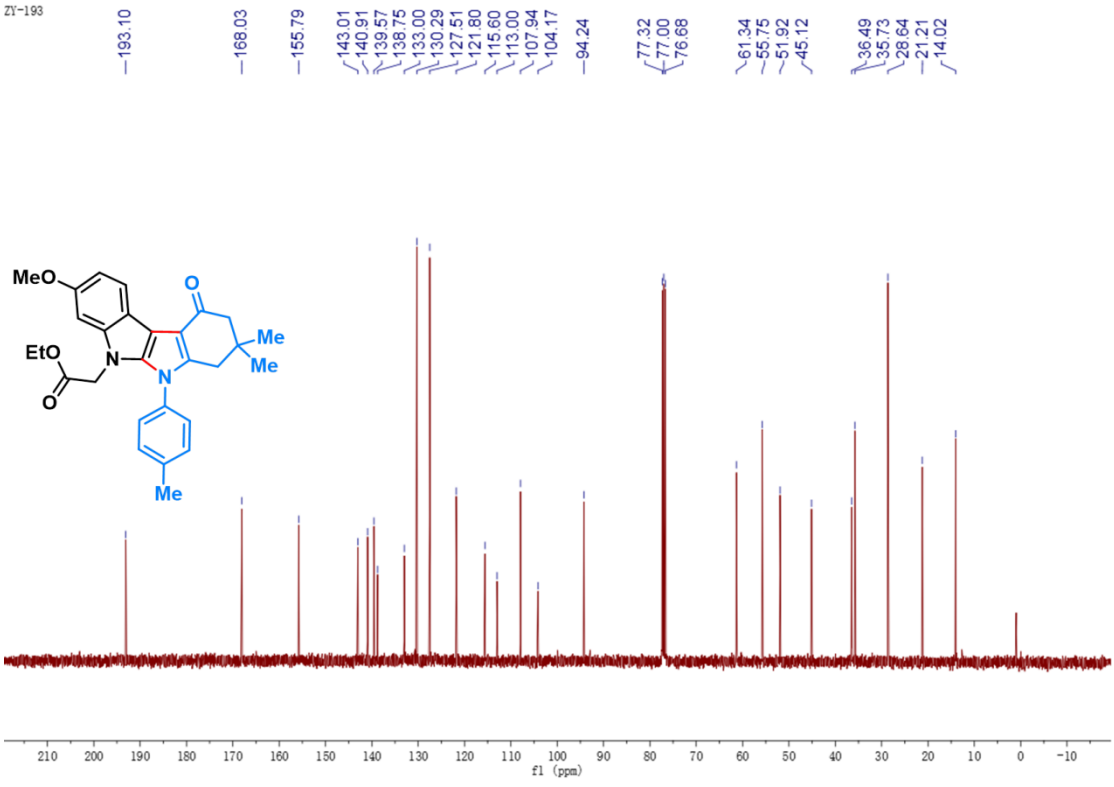
^{13}C NMR spectra of **3i**



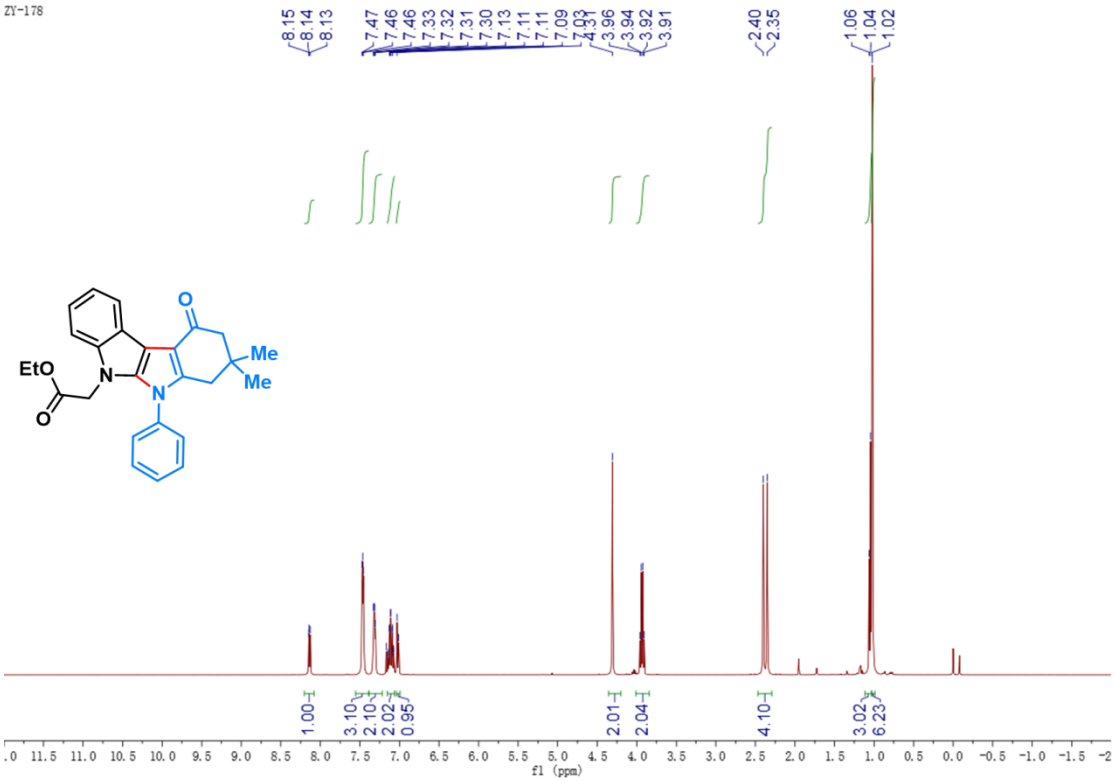
^{1}H NMR spectra of **3j**



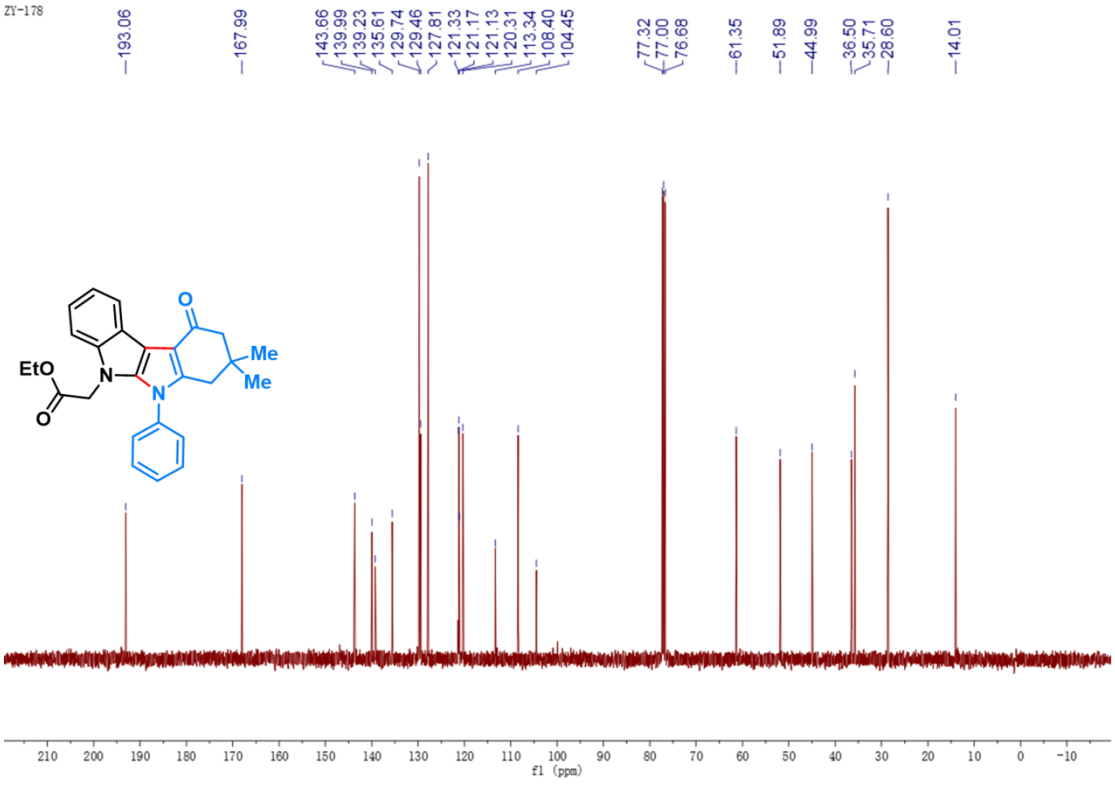
^{13}C NMR spectra of **3j**



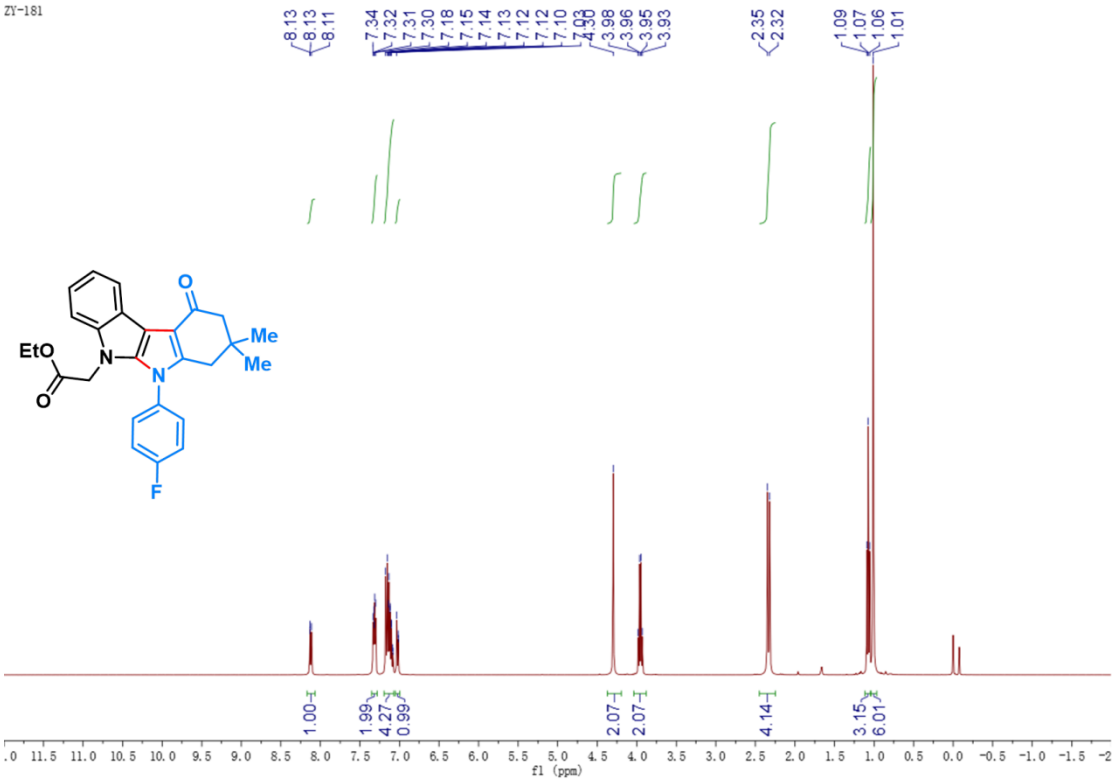
^{1}H NMR spectra of **3k**



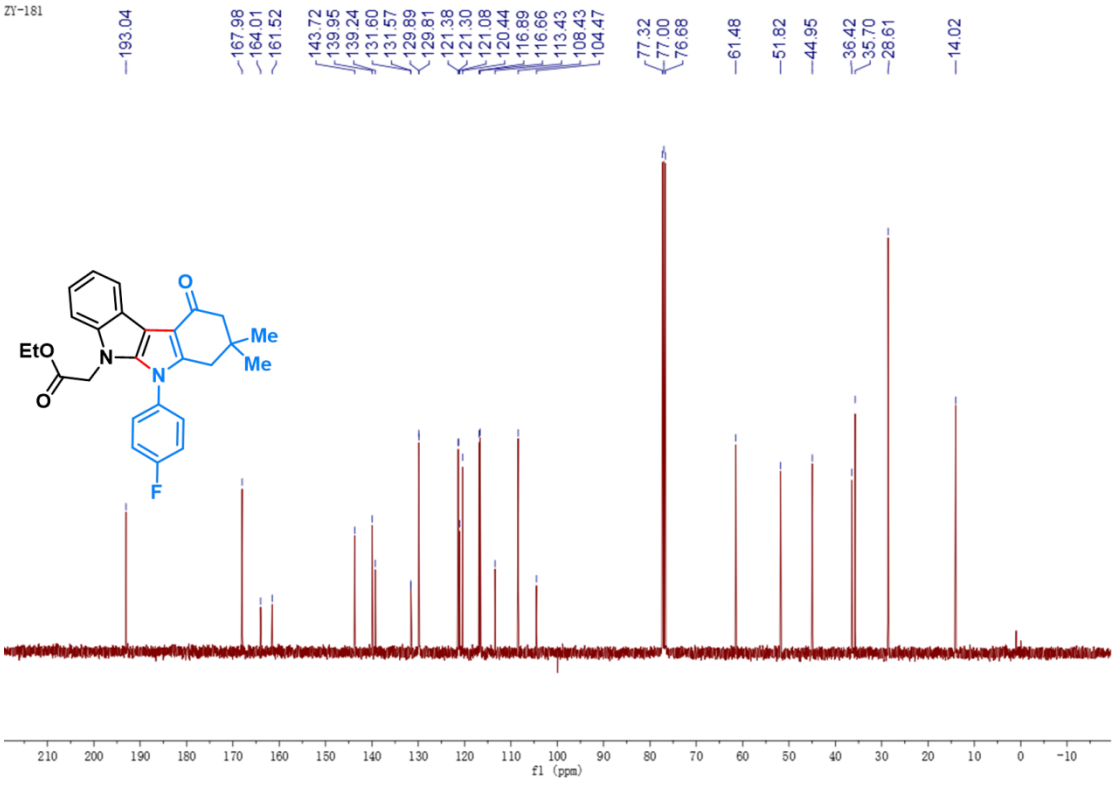
^{13}C NMR spectra of **3k**



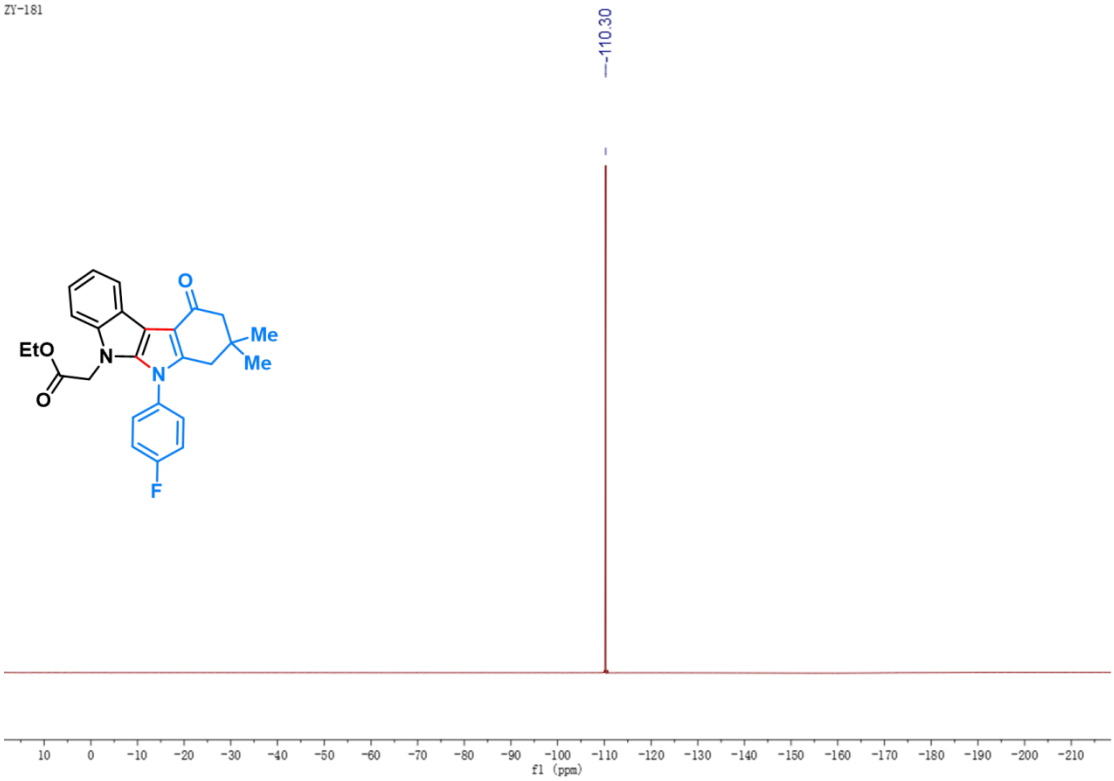
^{1}H NMR spectra of **3l**



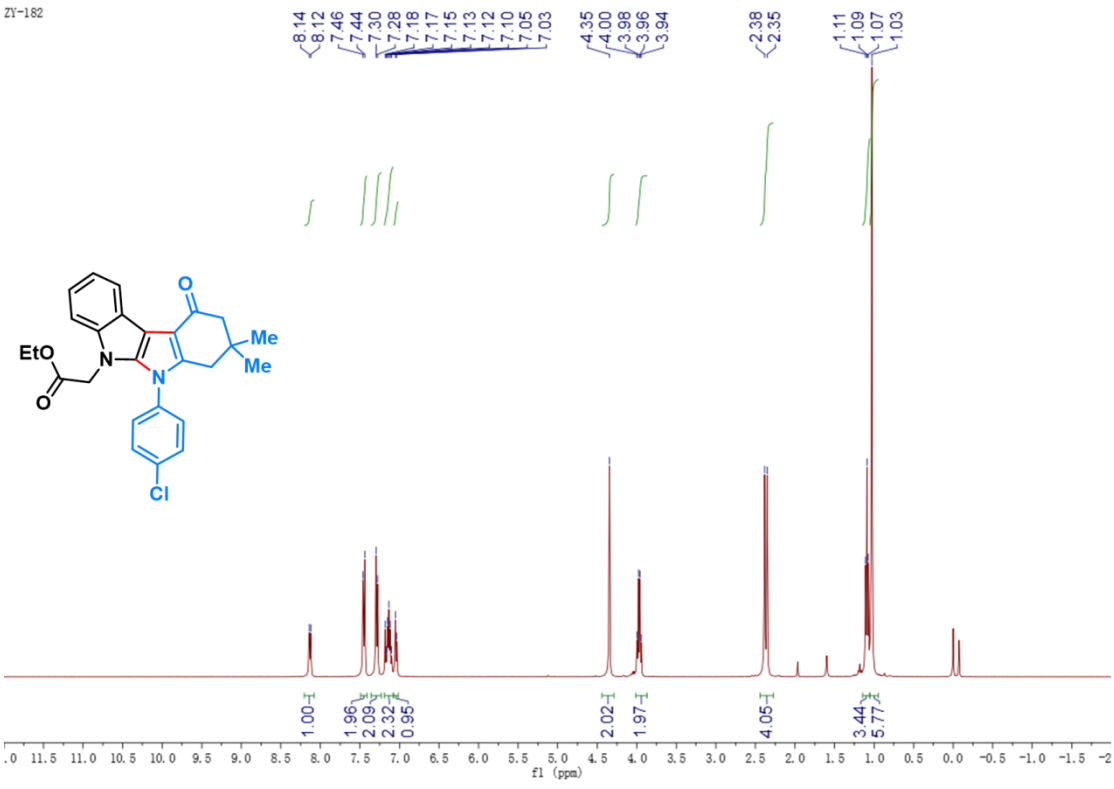
^{13}C NMR spectra of **3l**



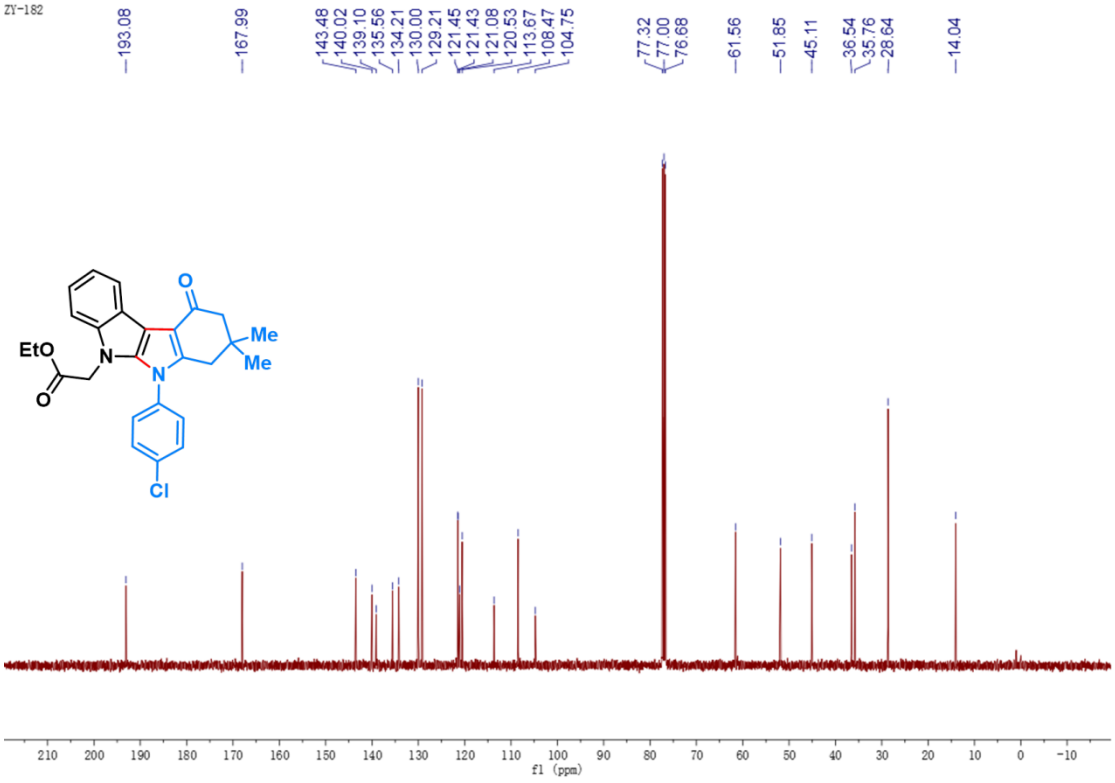
^{19}F NMR spectra of **3l**



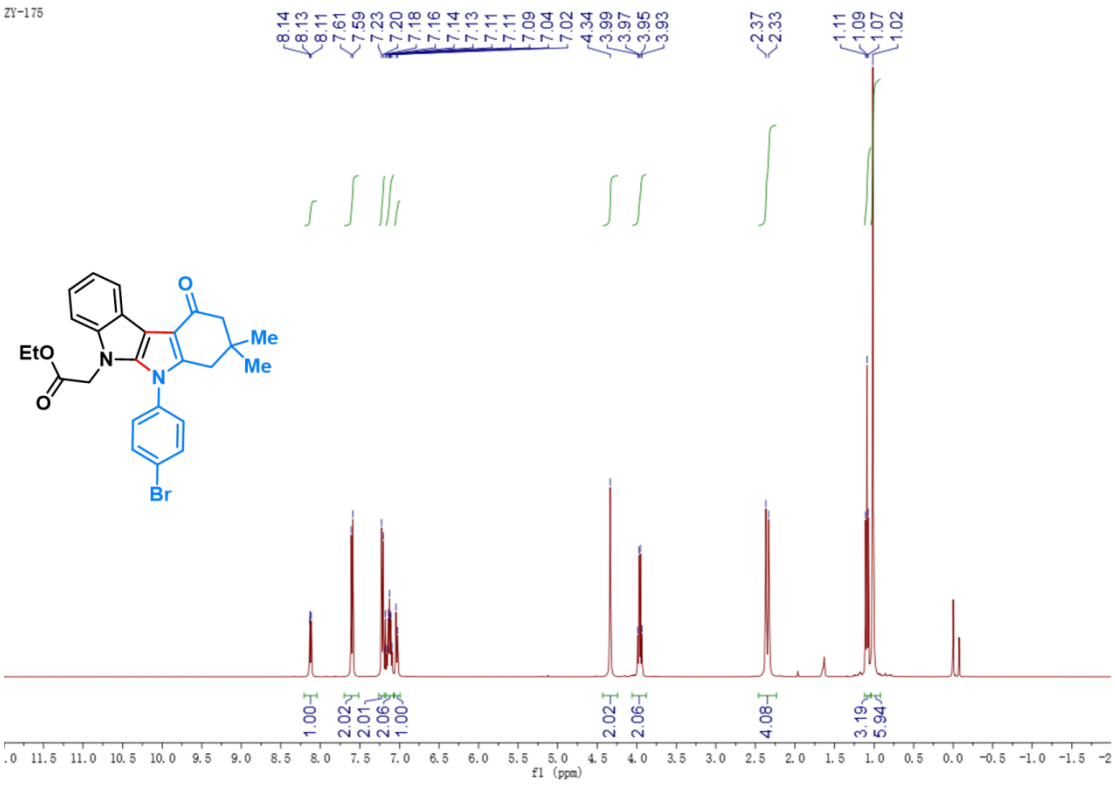
^{1}H NMR spectra of **3m**



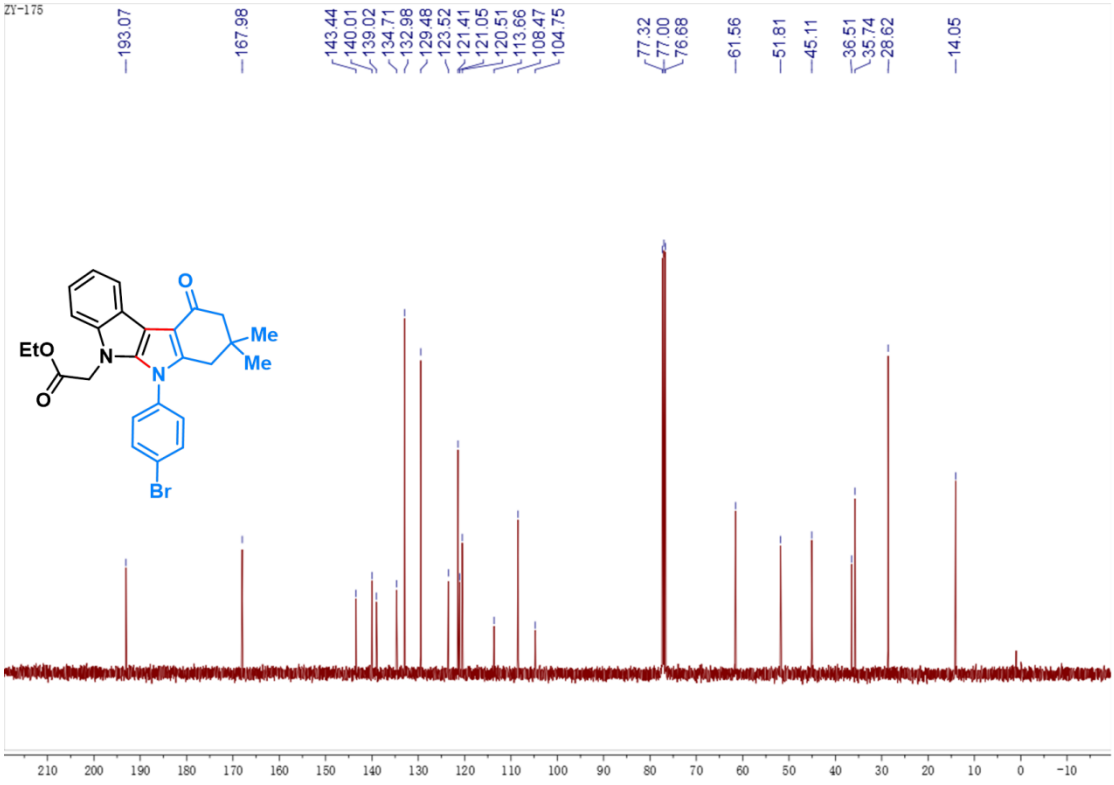
^{13}C NMR spectra of **3m**



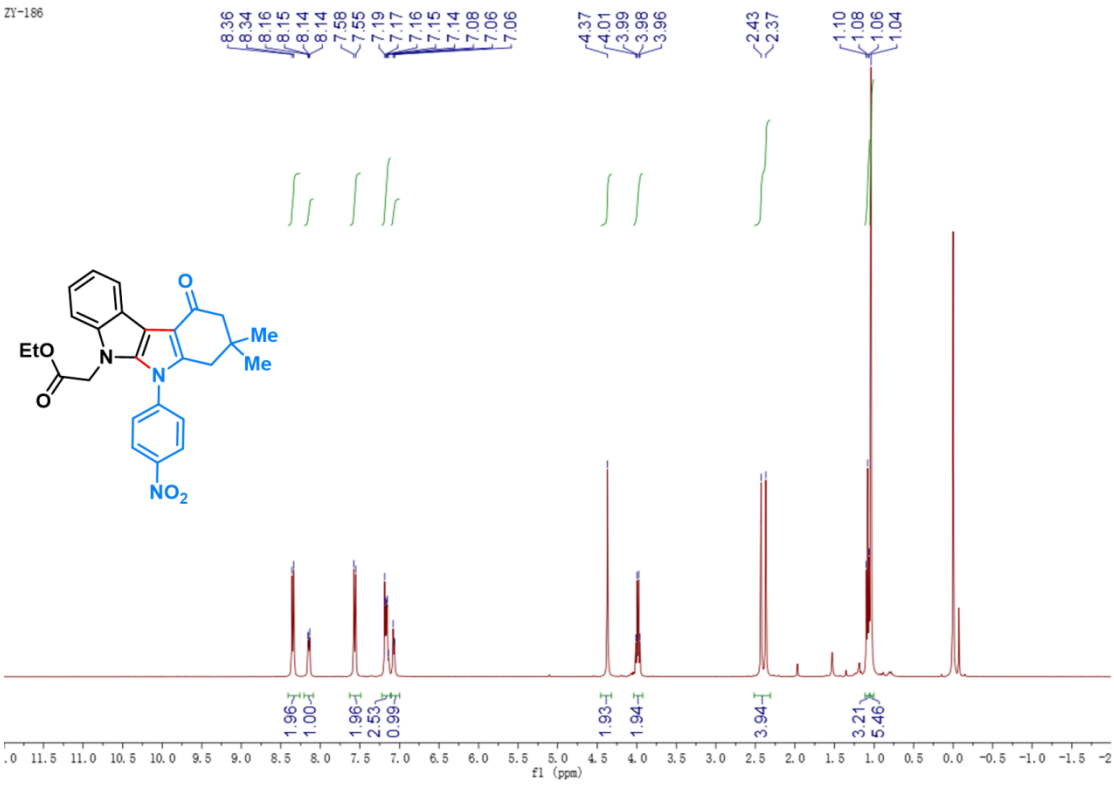
^{1}H NMR spectra of **3n**



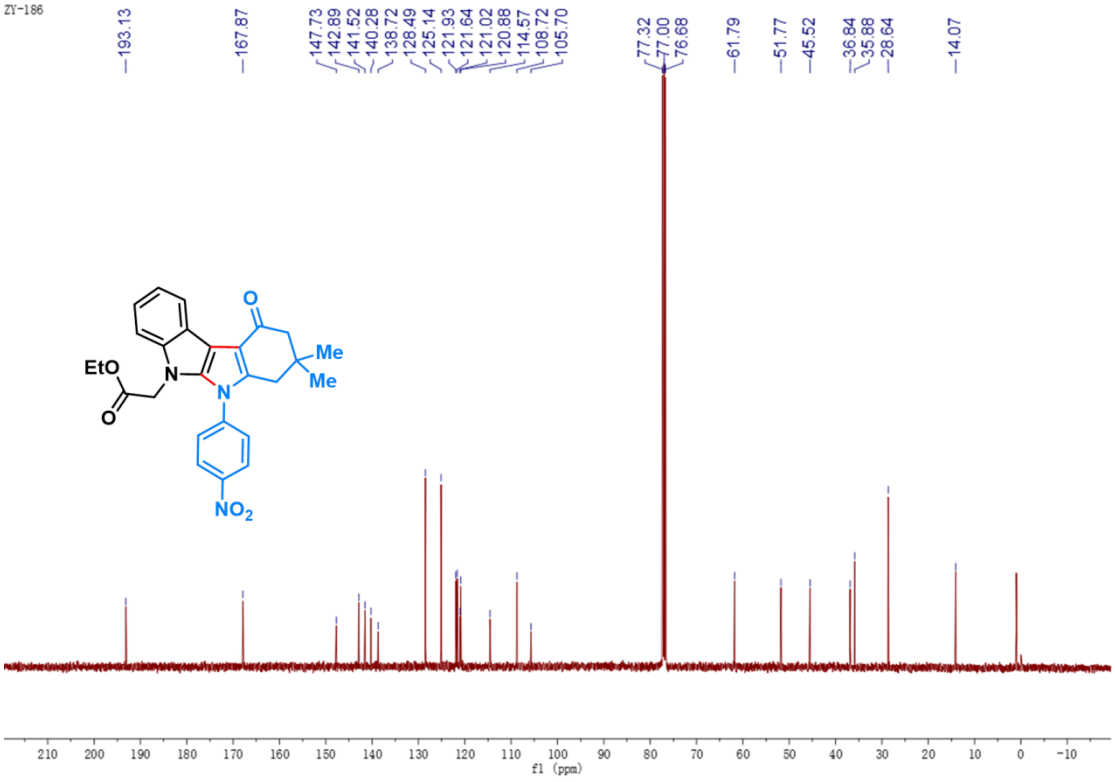
^{13}C NMR spectra of **3n**



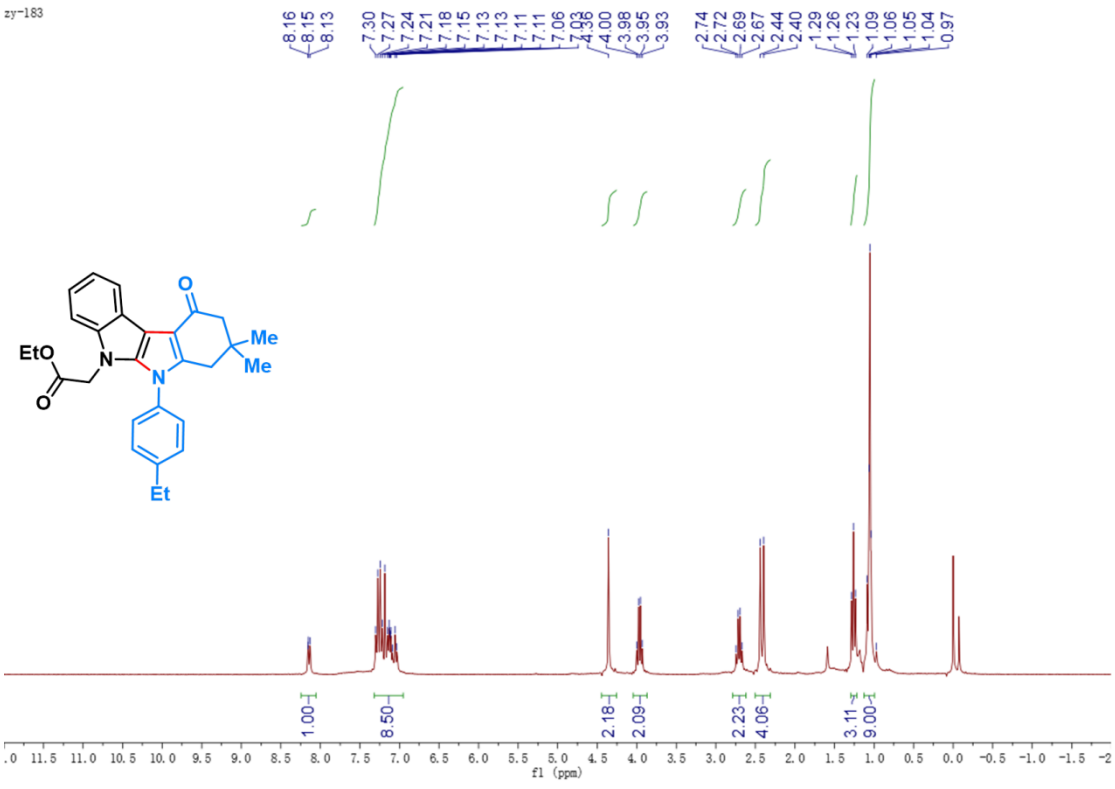
^{1}H NMR spectra of **3o**



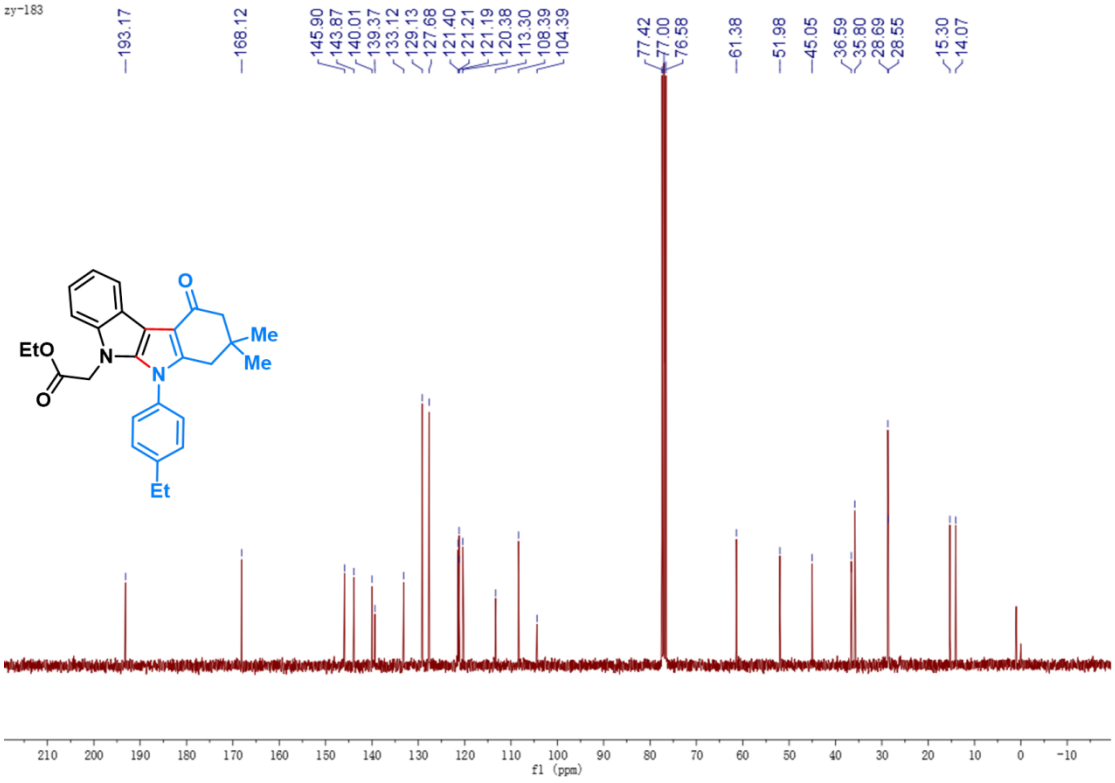
^{13}C NMR spectra of **3o**



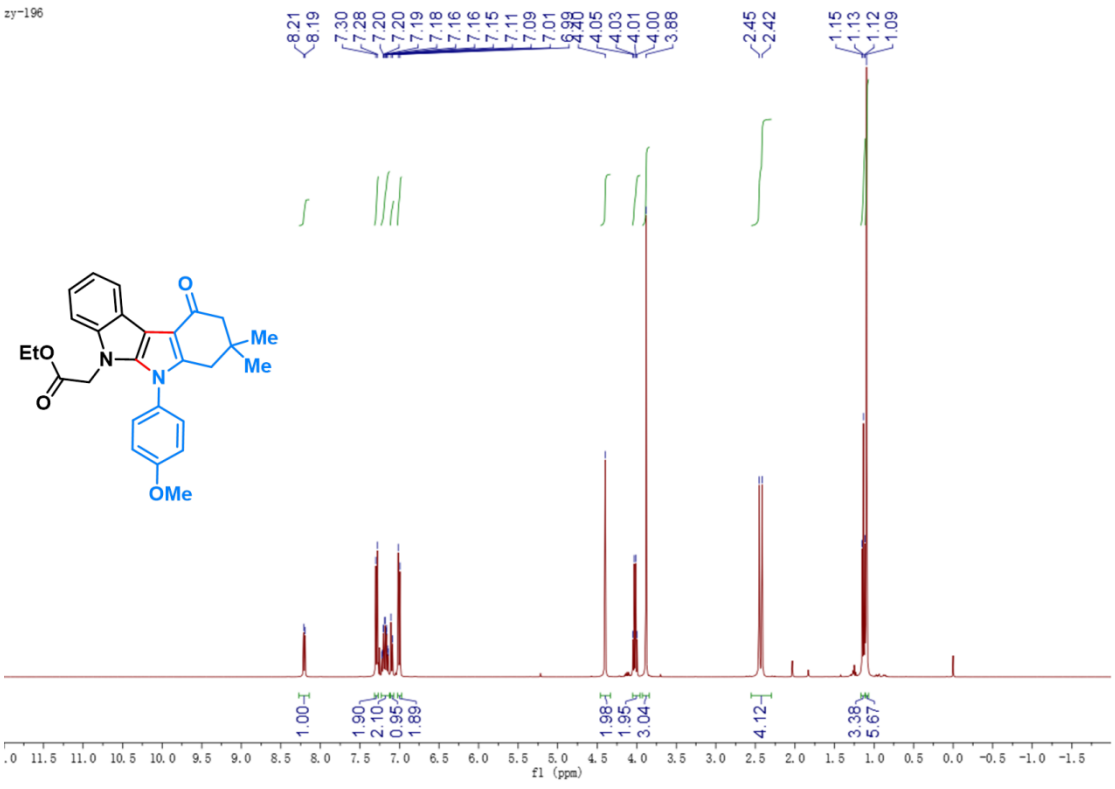
^{1}H NMR spectra of **3p**



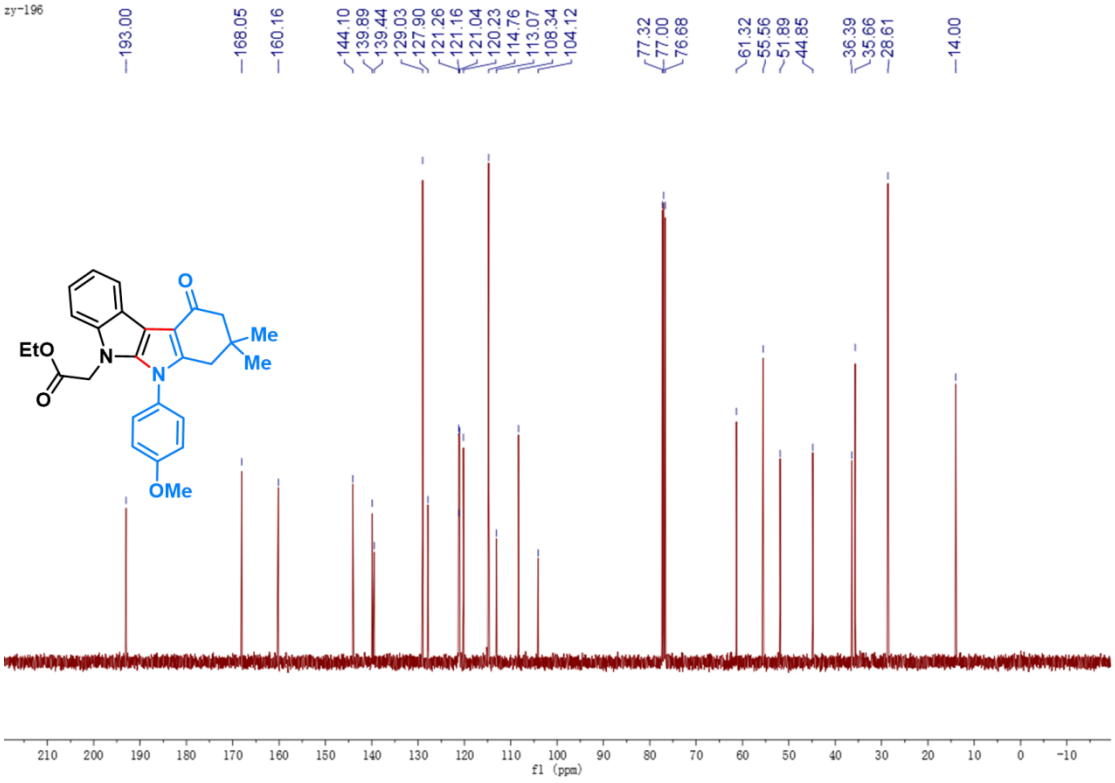
^{13}C NMR spectra of **3p**



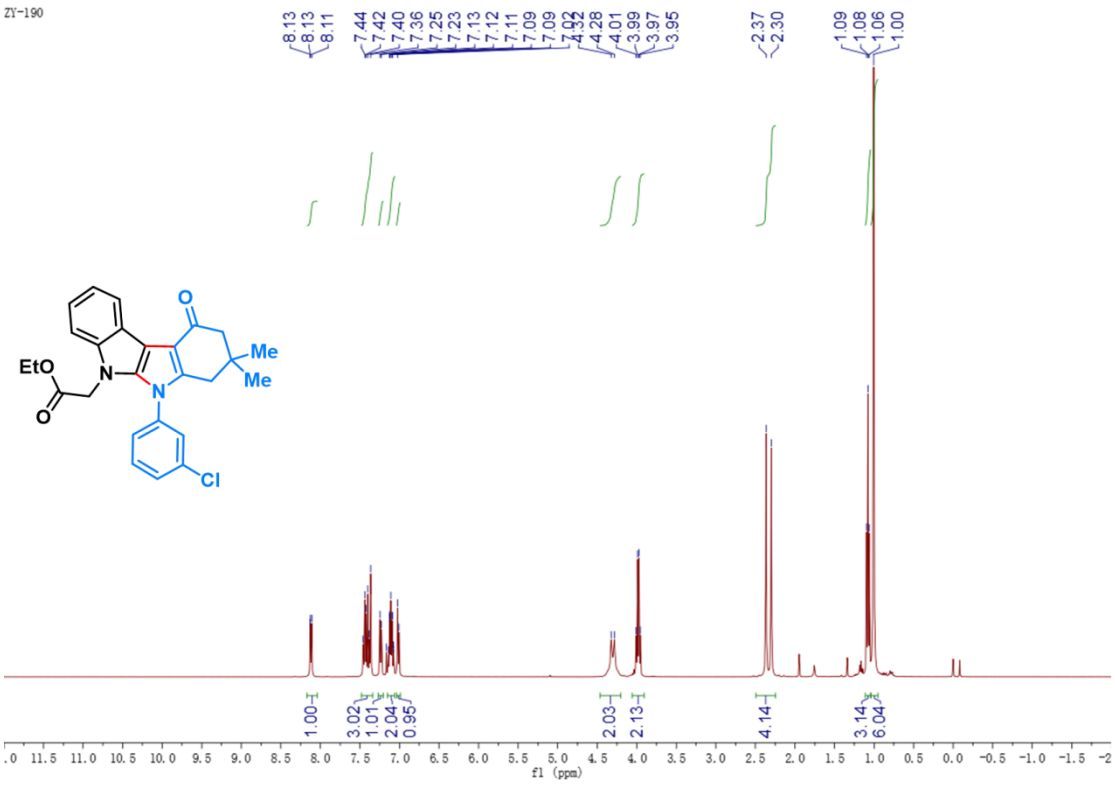
^{1}H NMR spectra of **3q**



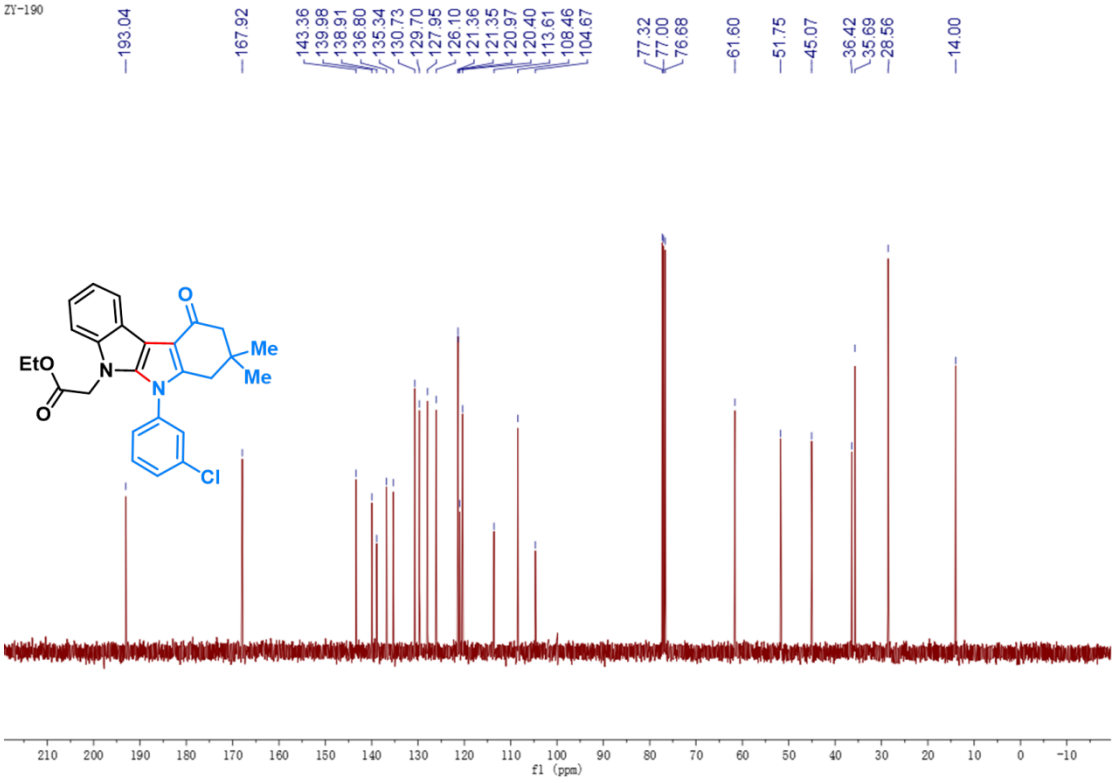
^{13}C NMR spectra of **3q**



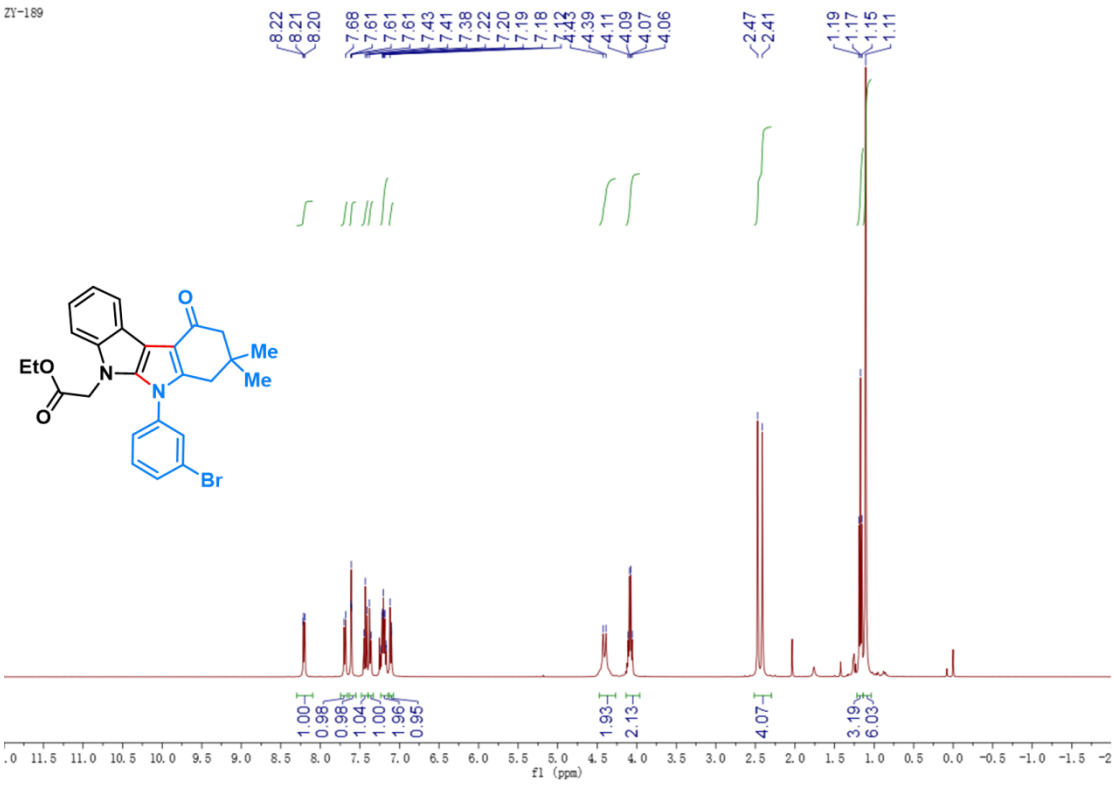
^{1}H NMR spectra of **3r**



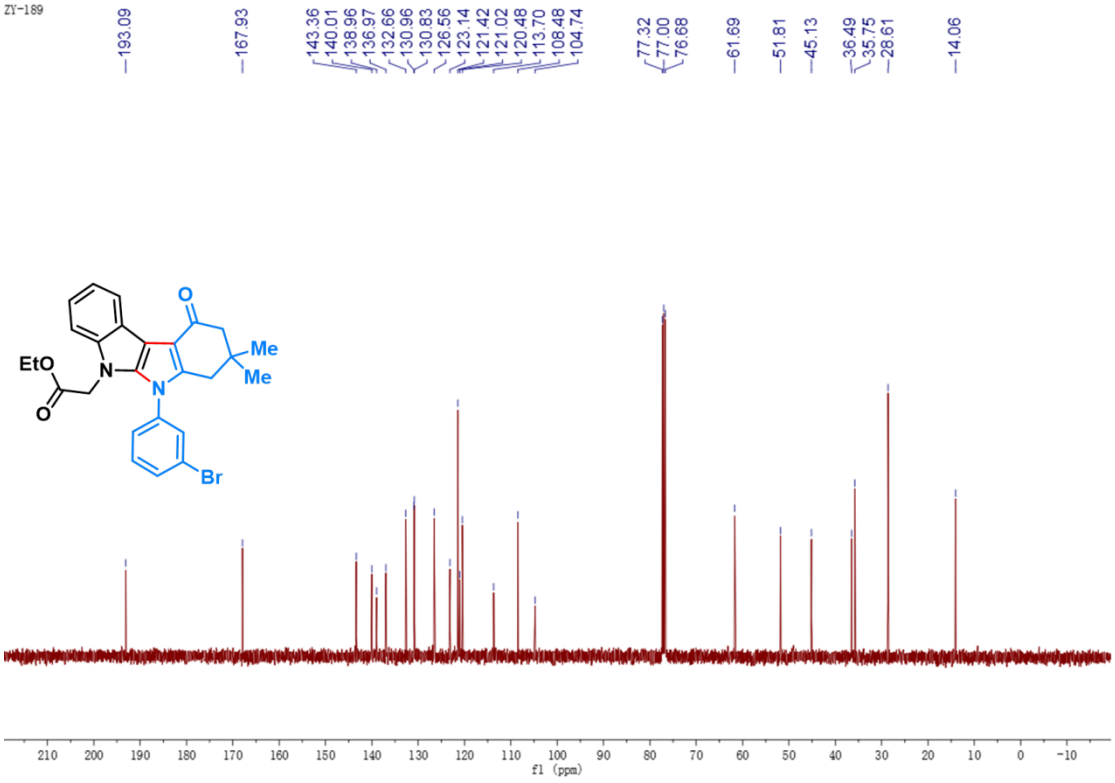
^{13}C NMR spectra of **3r**



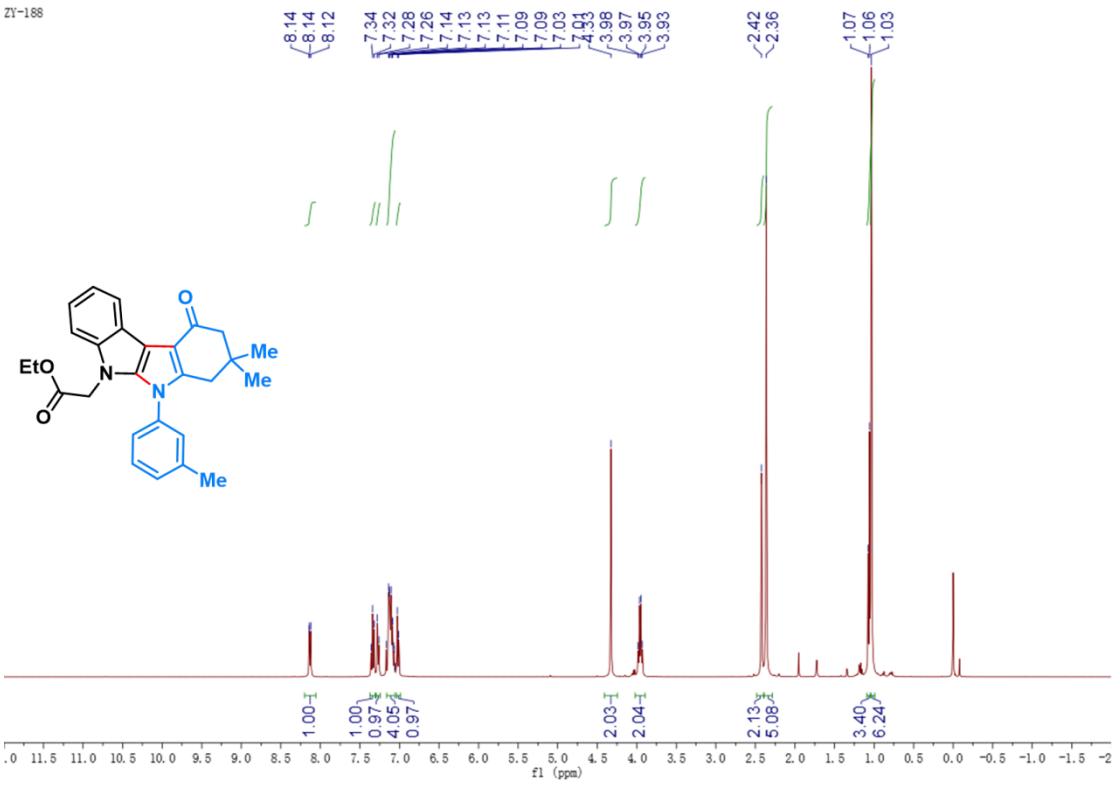
^{1}H NMR spectra of **3s**



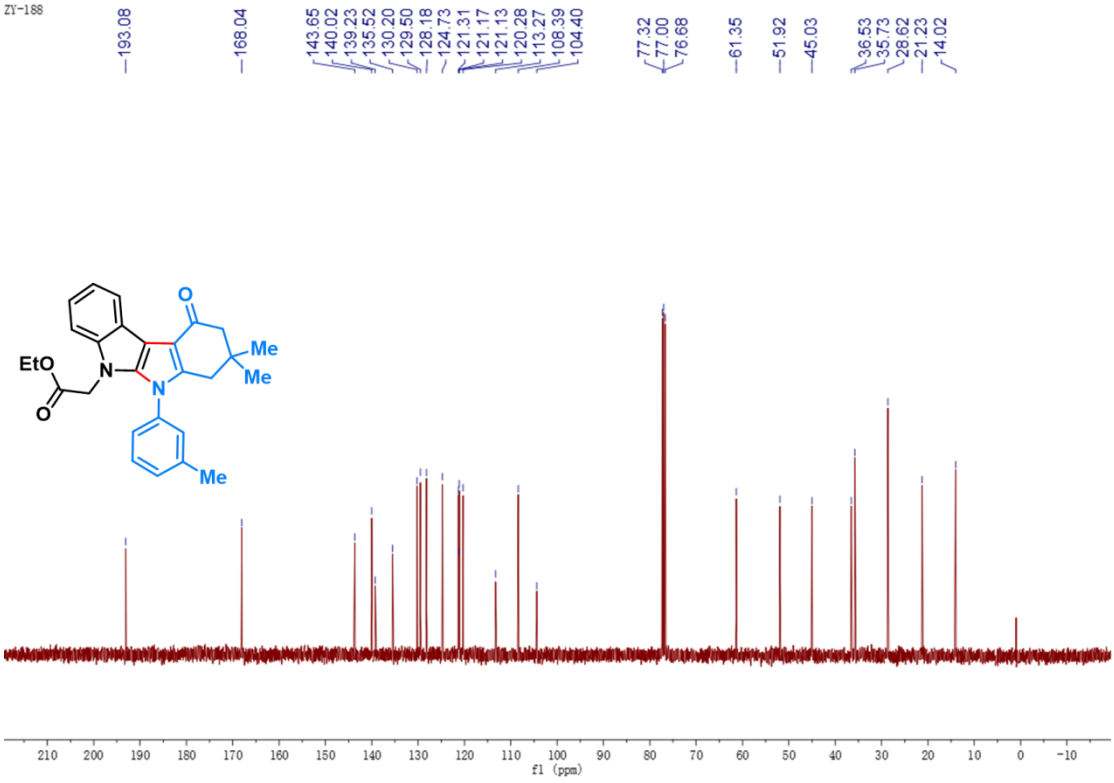
^{13}C NMR spectra of **3s**



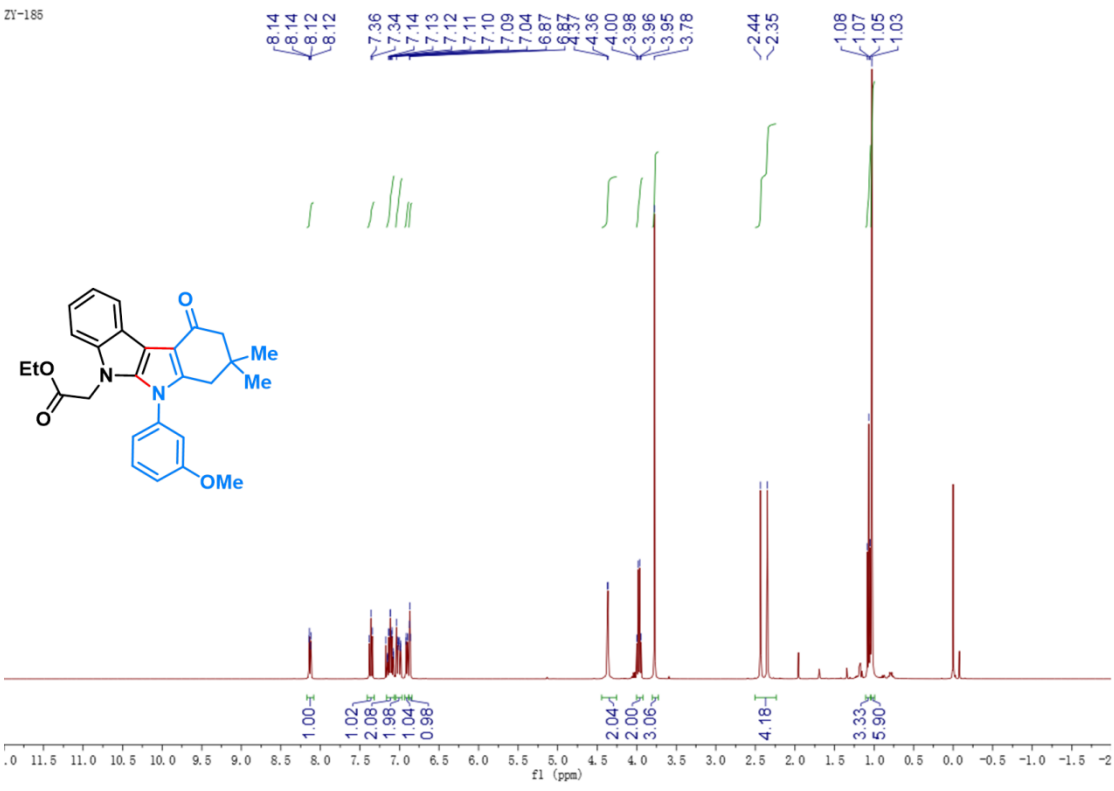
^{1}H NMR spectra of **3t**



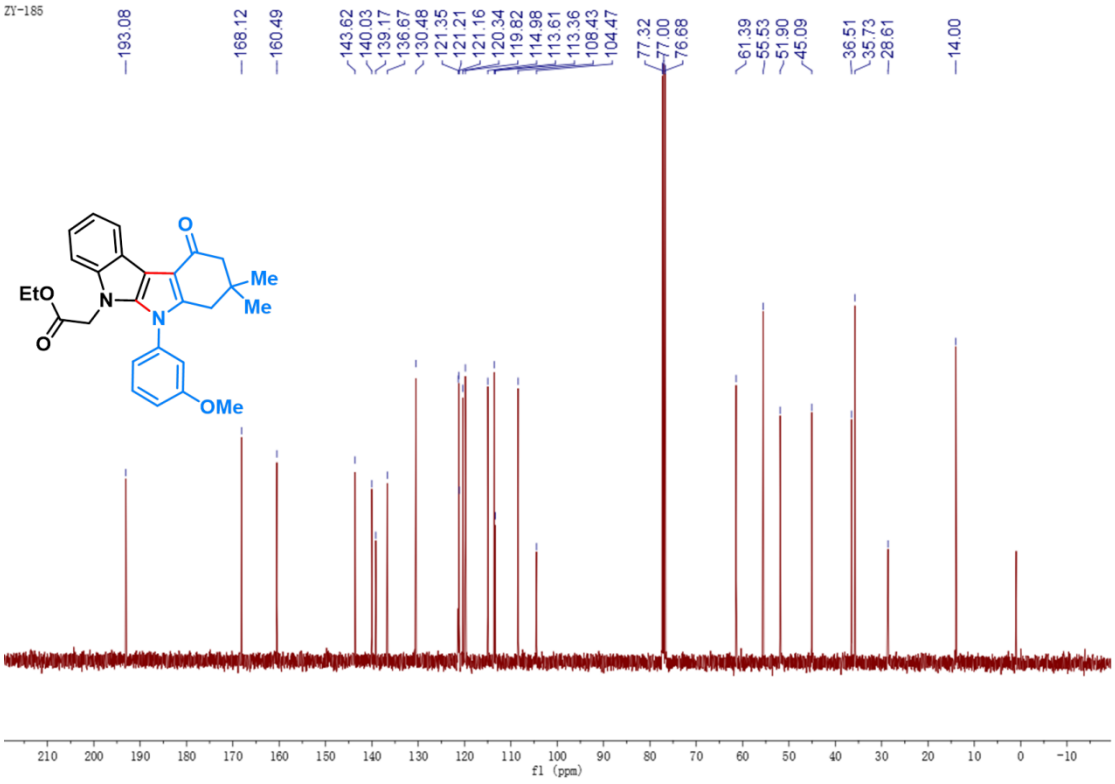
^{13}C NMR spectra of **3t**



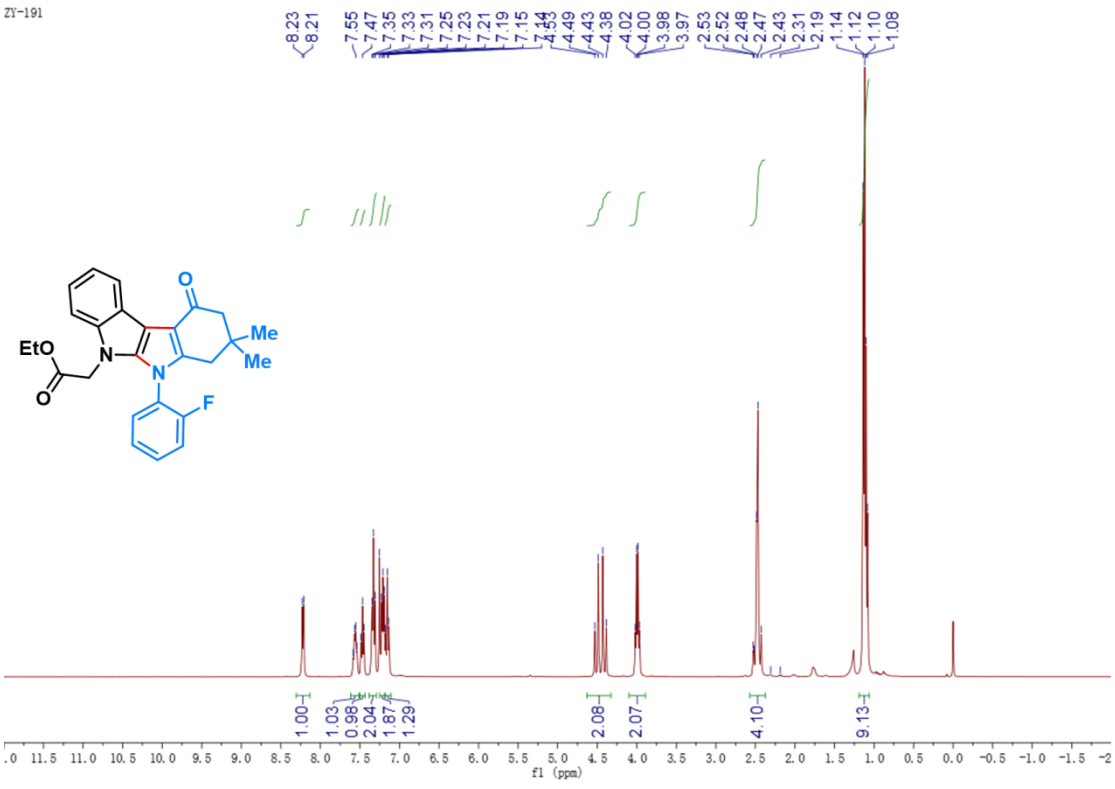
^{1}H NMR spectra of **3u**



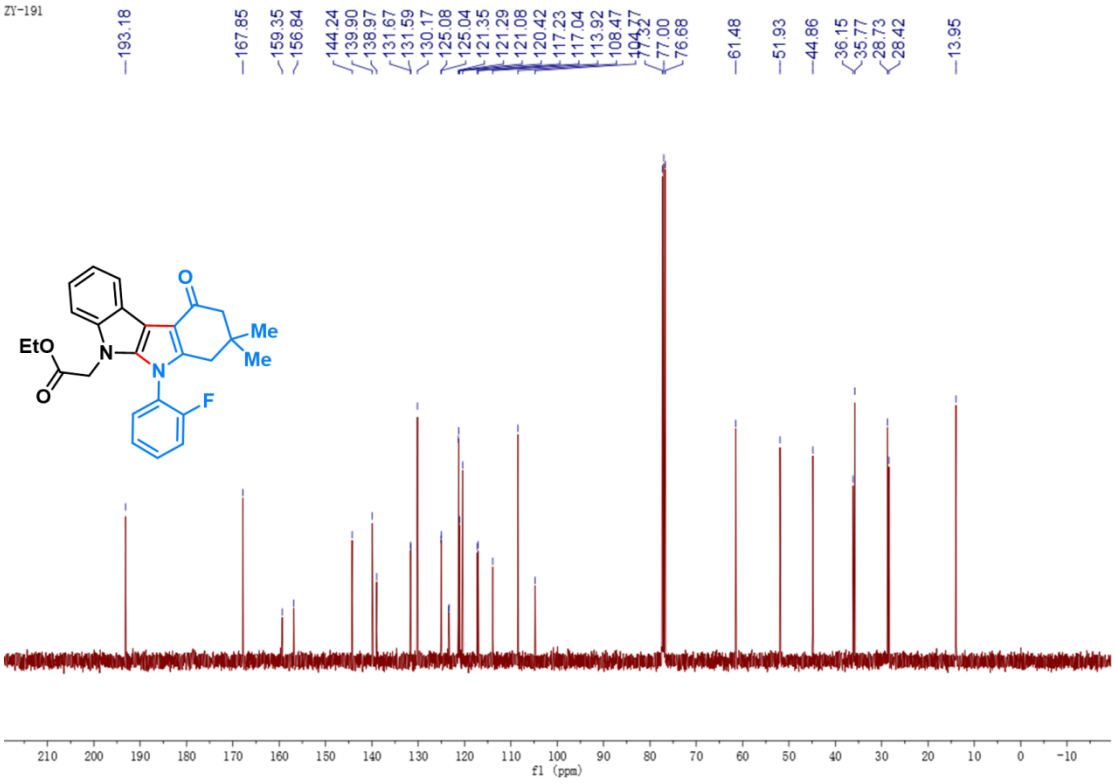
^{13}C NMR spectra of **3u**



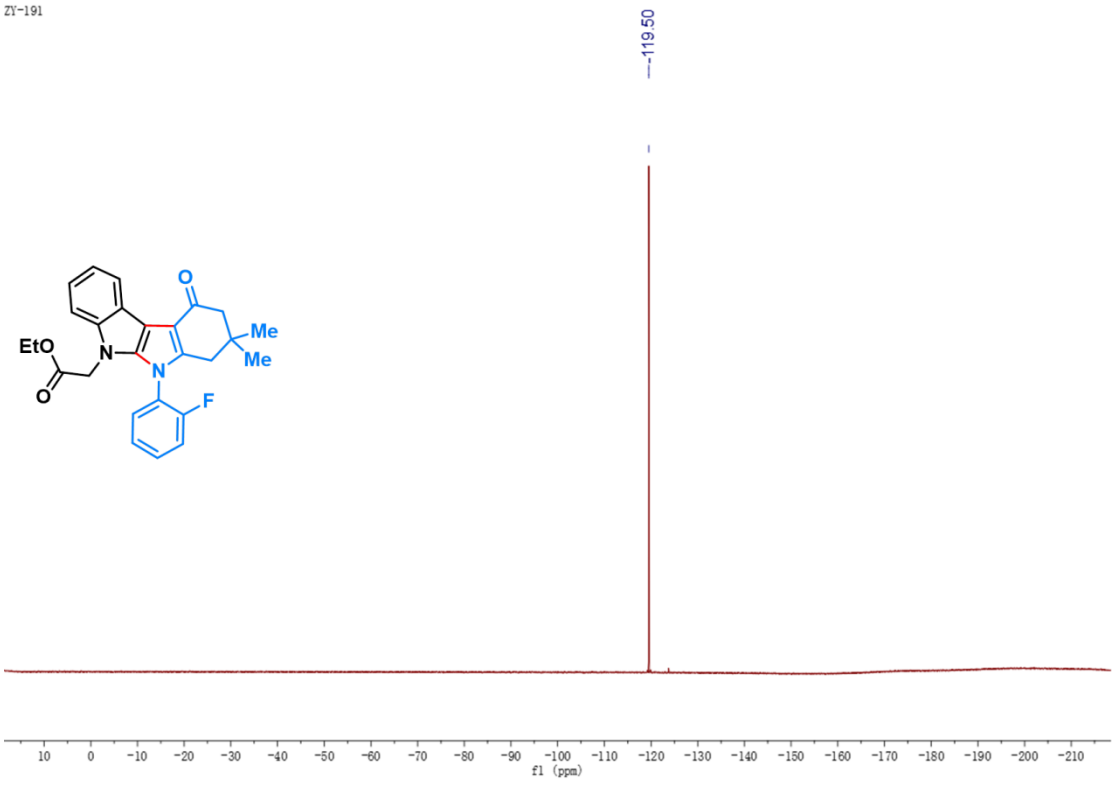
^{1}H NMR spectra of **3v**



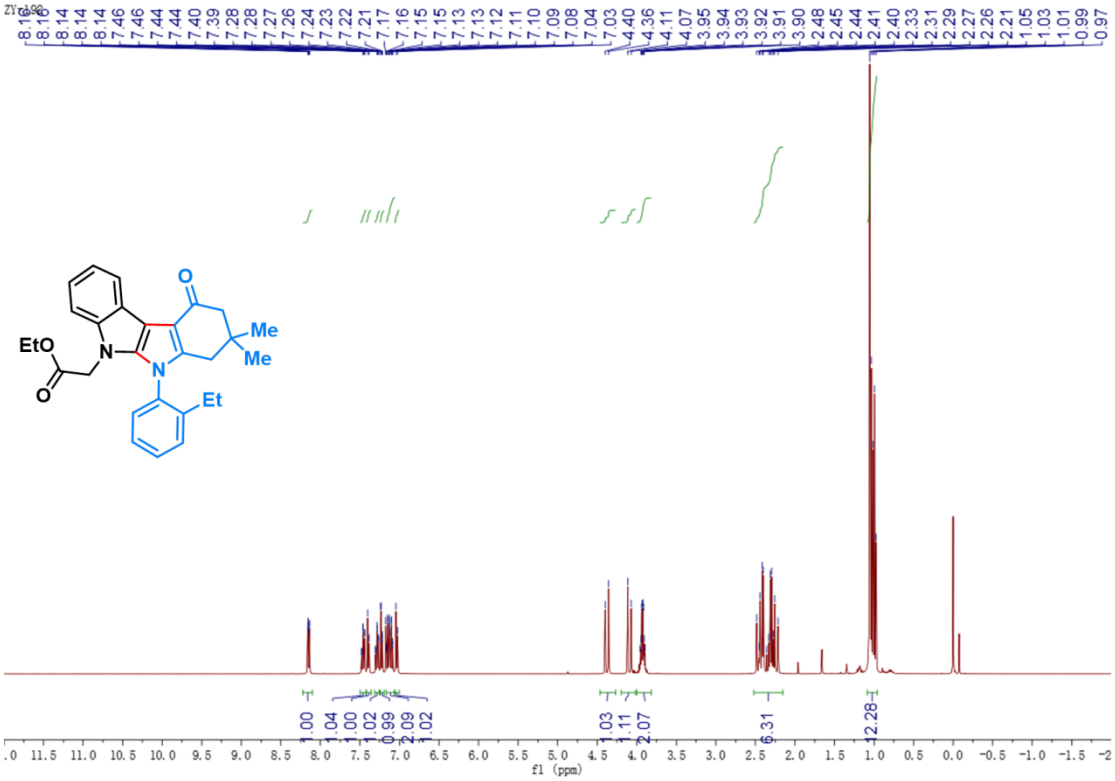
^{13}C NMR spectra of **3v**



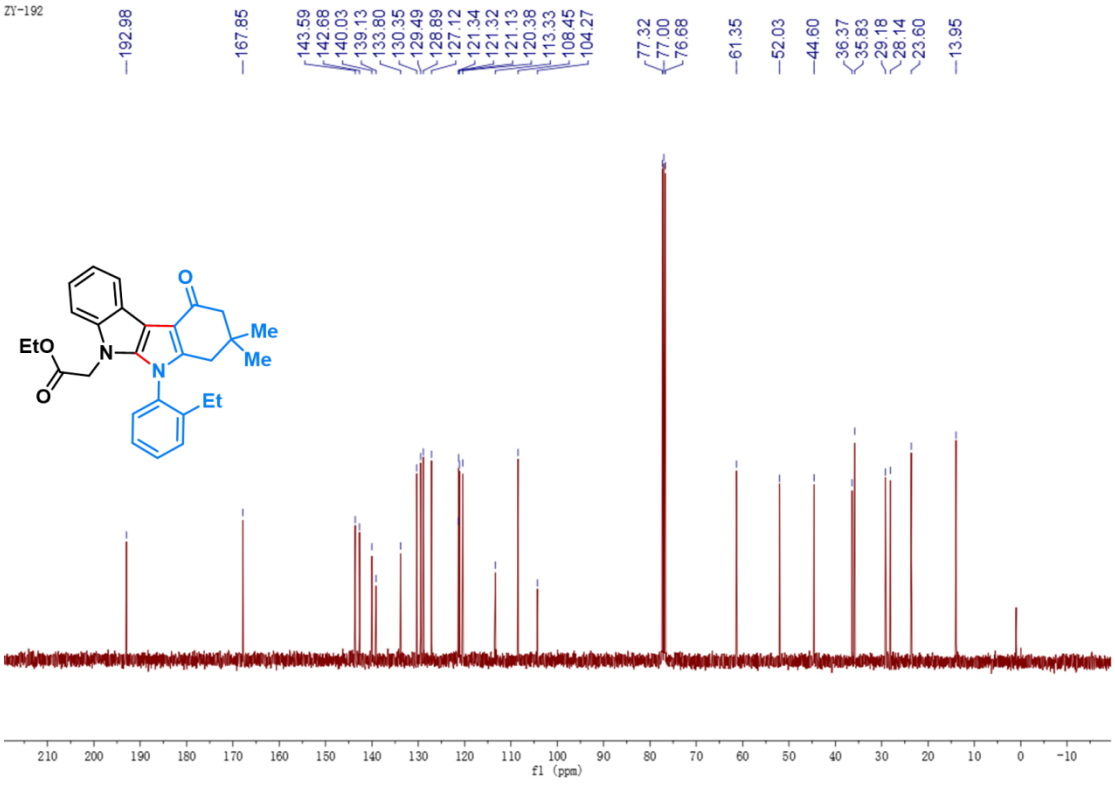
^{19}F NMR spectra of **3v**



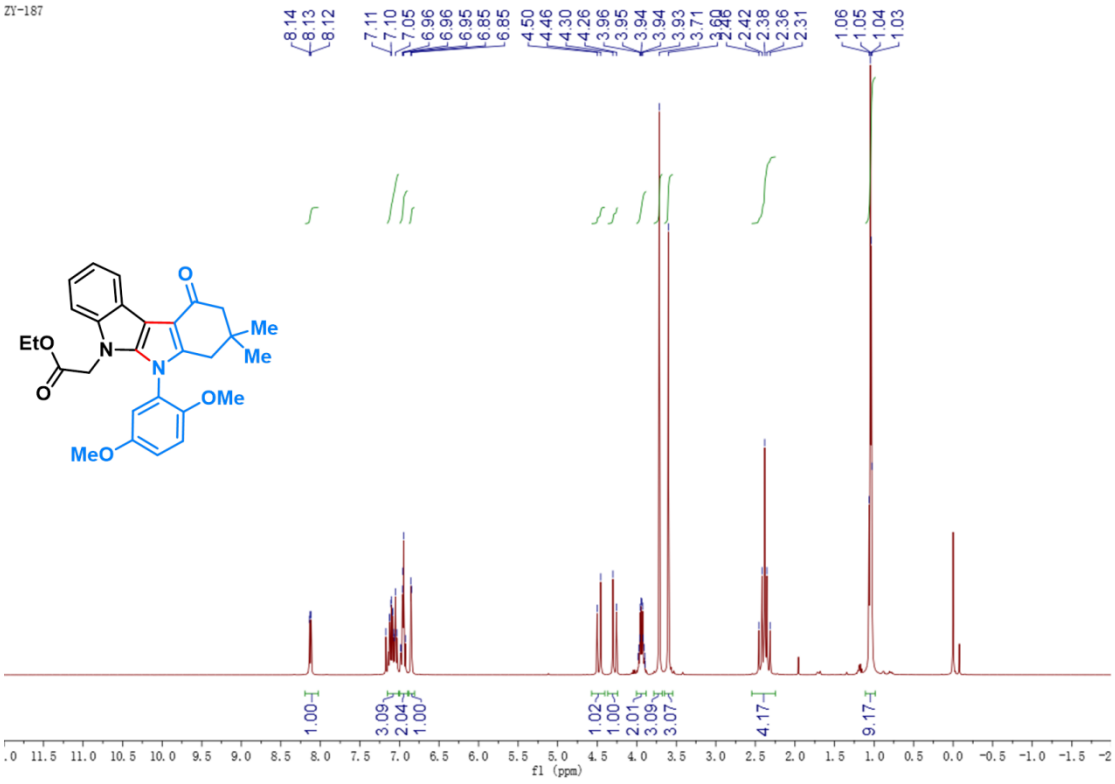
^{1}H NMR spectra of **3w**



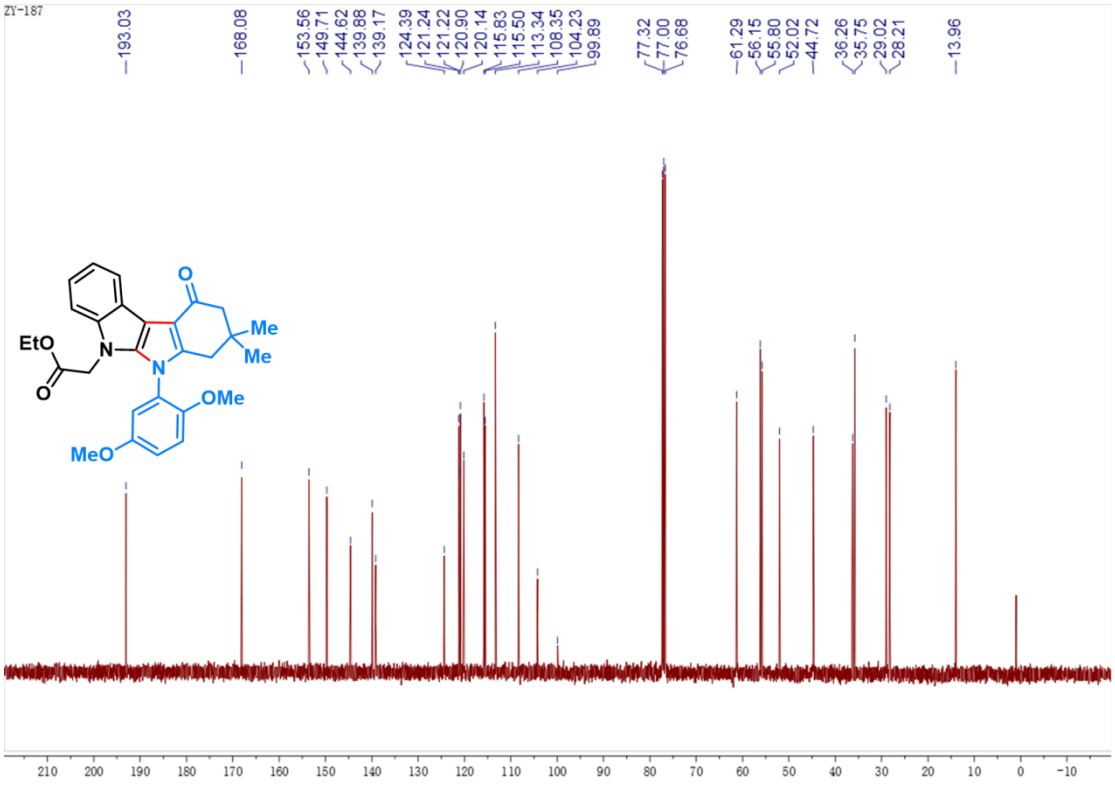
^{13}C NMR spectra of **3w**



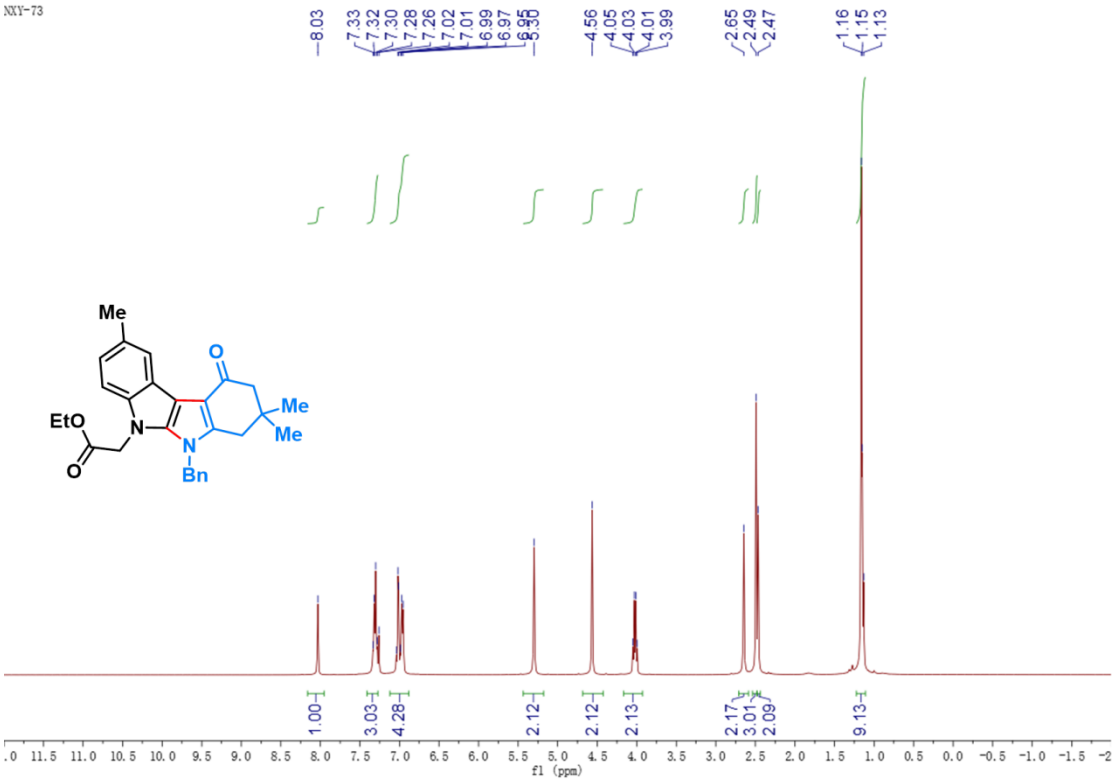
^{1}H NMR spectra of **3x**



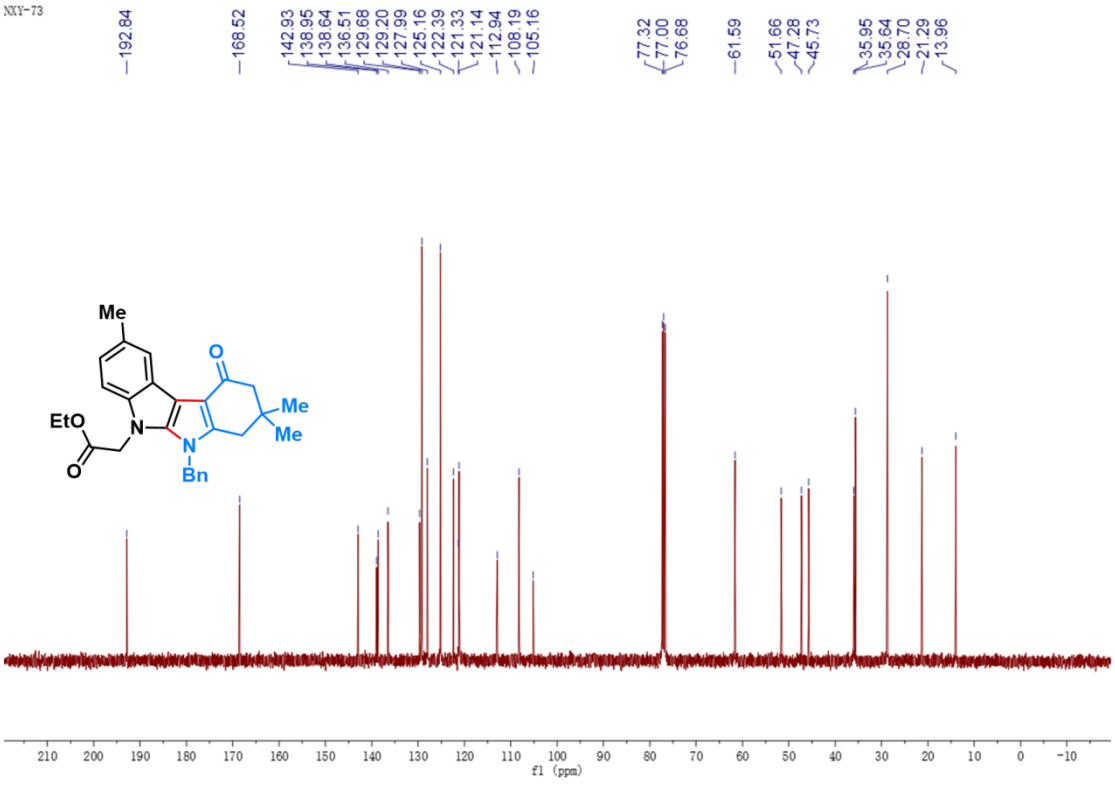
^{13}C NMR spectra of **3x**



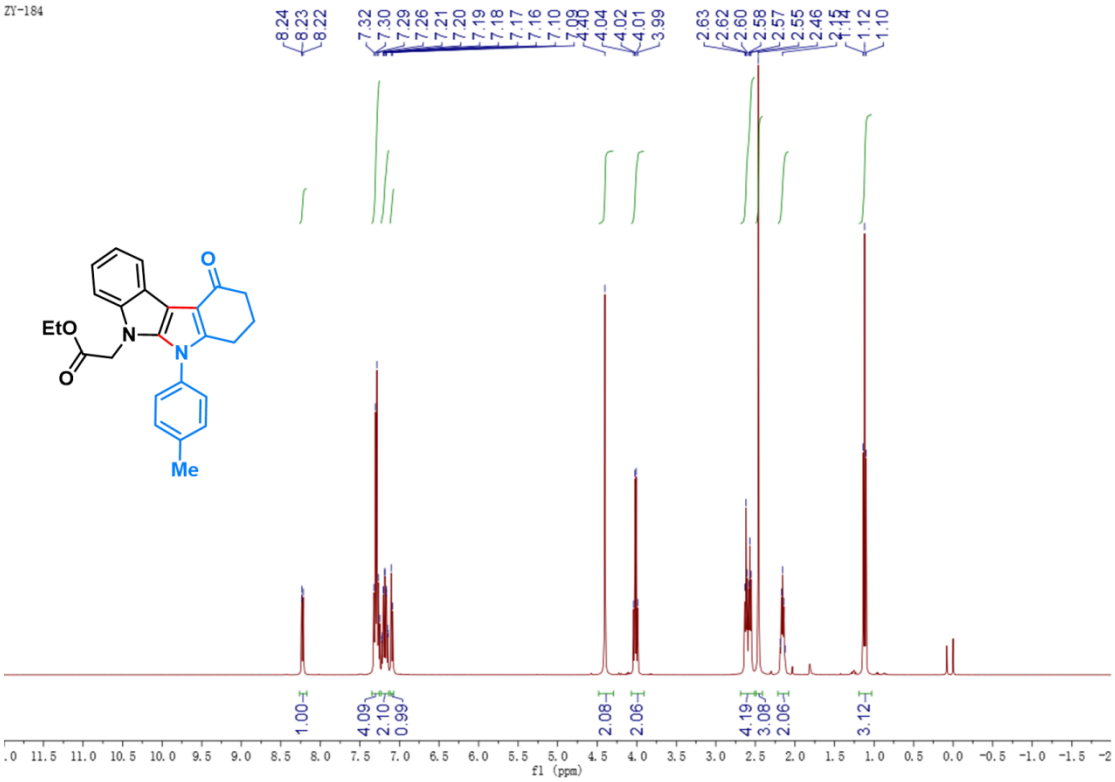
^{1}H NMR spectra of **3y**



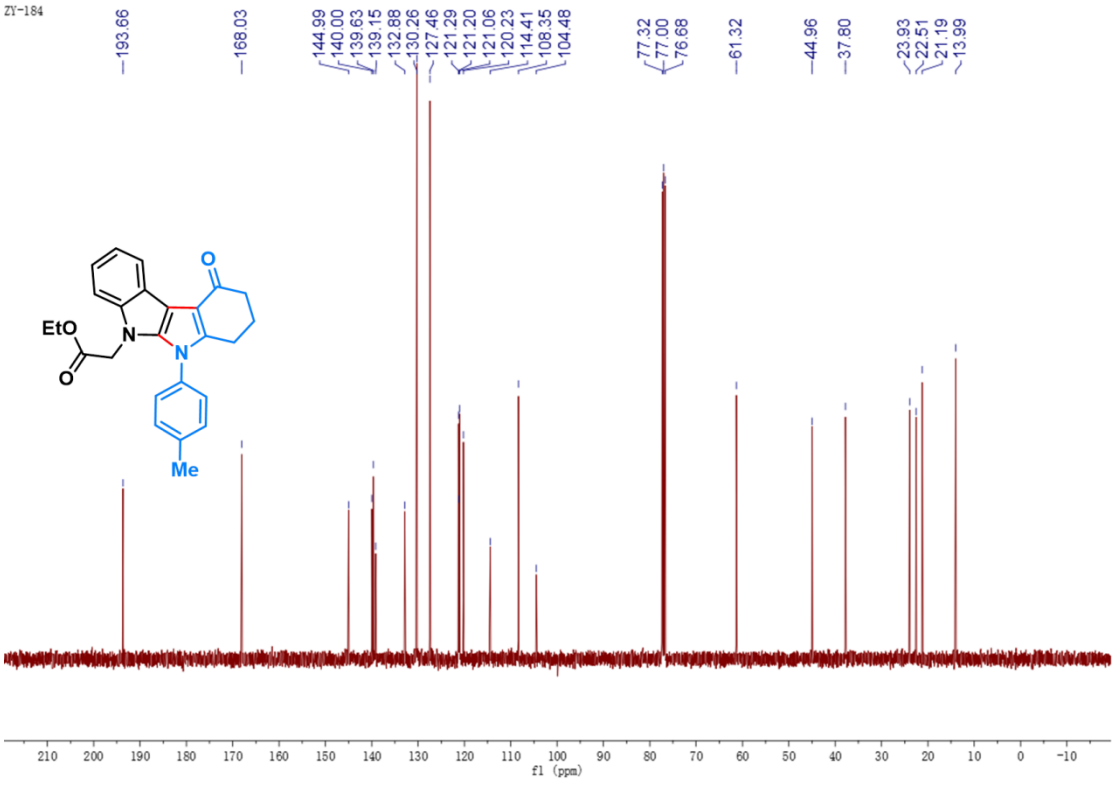
^{13}C NMR spectra of **3y**



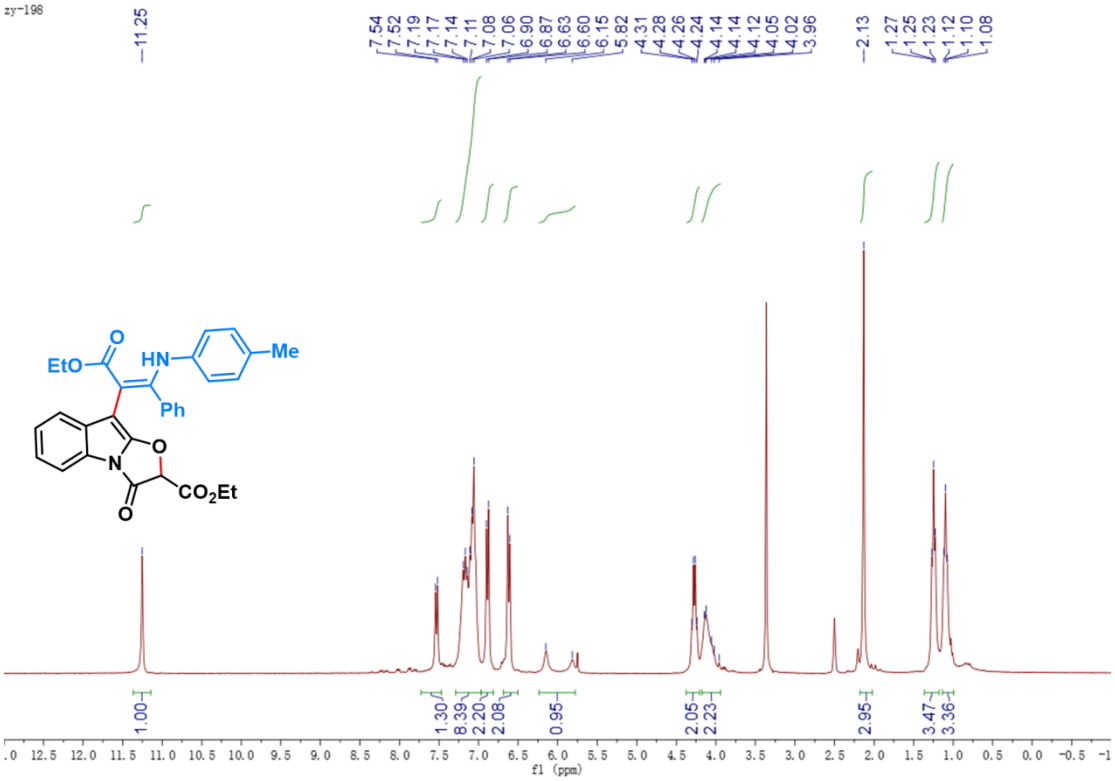
^{1}H NMR spectra of **3z**



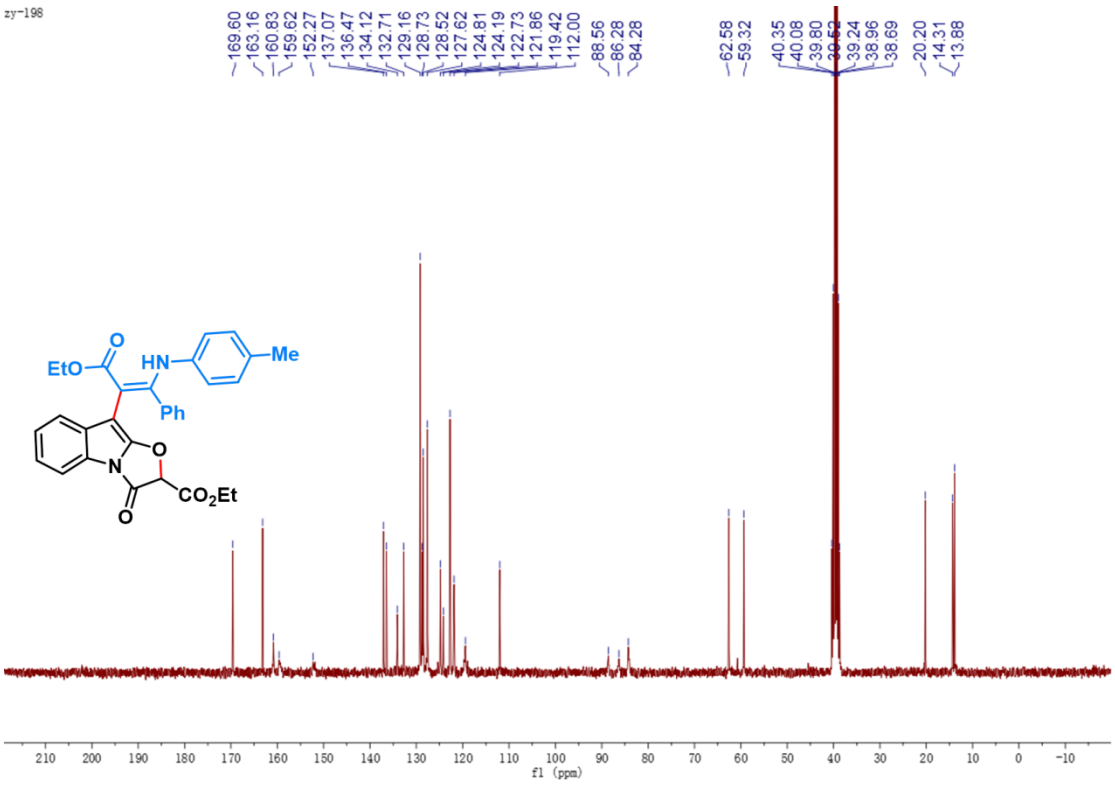
^{13}C NMR spectra of **3z**



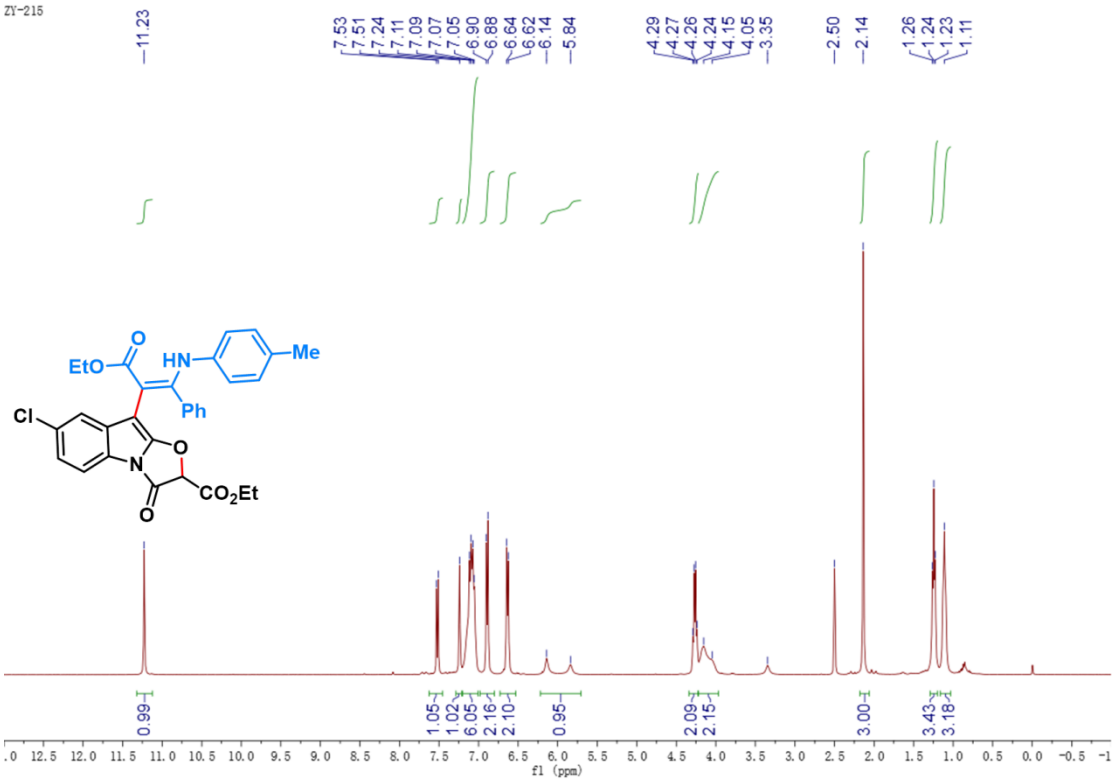
^{1}H NMR spectra of **5a**



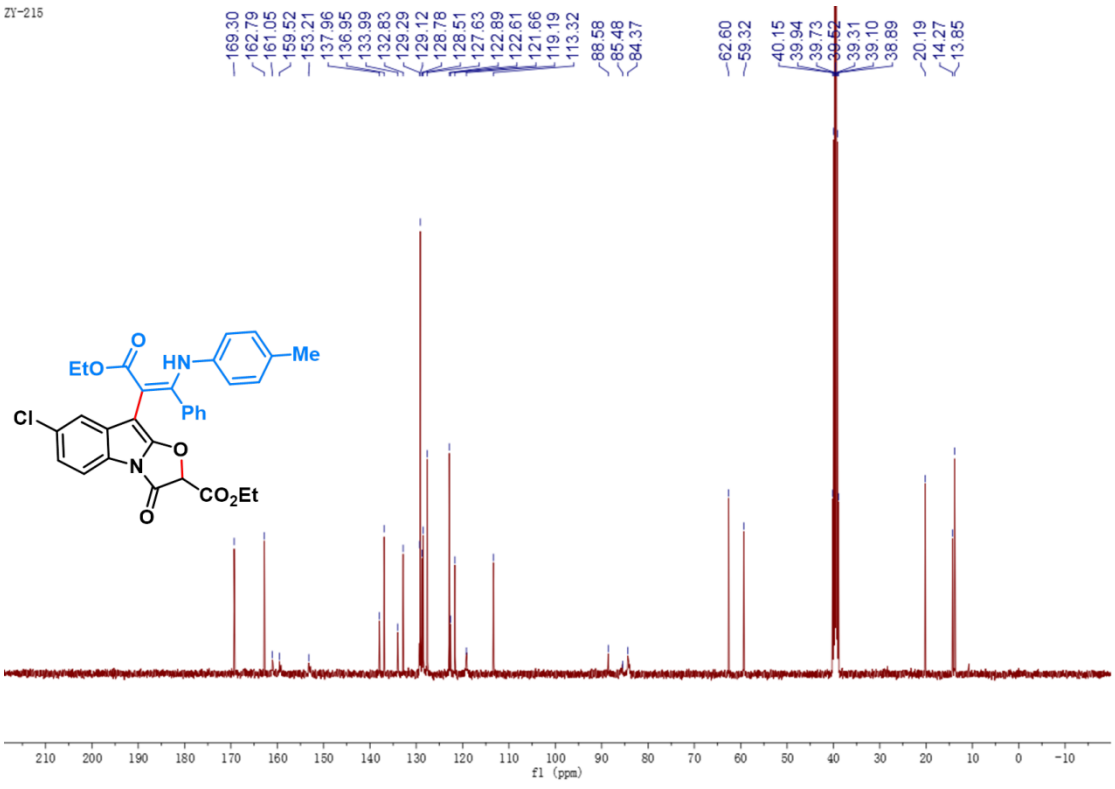
^{13}C NMR spectra of **5a**



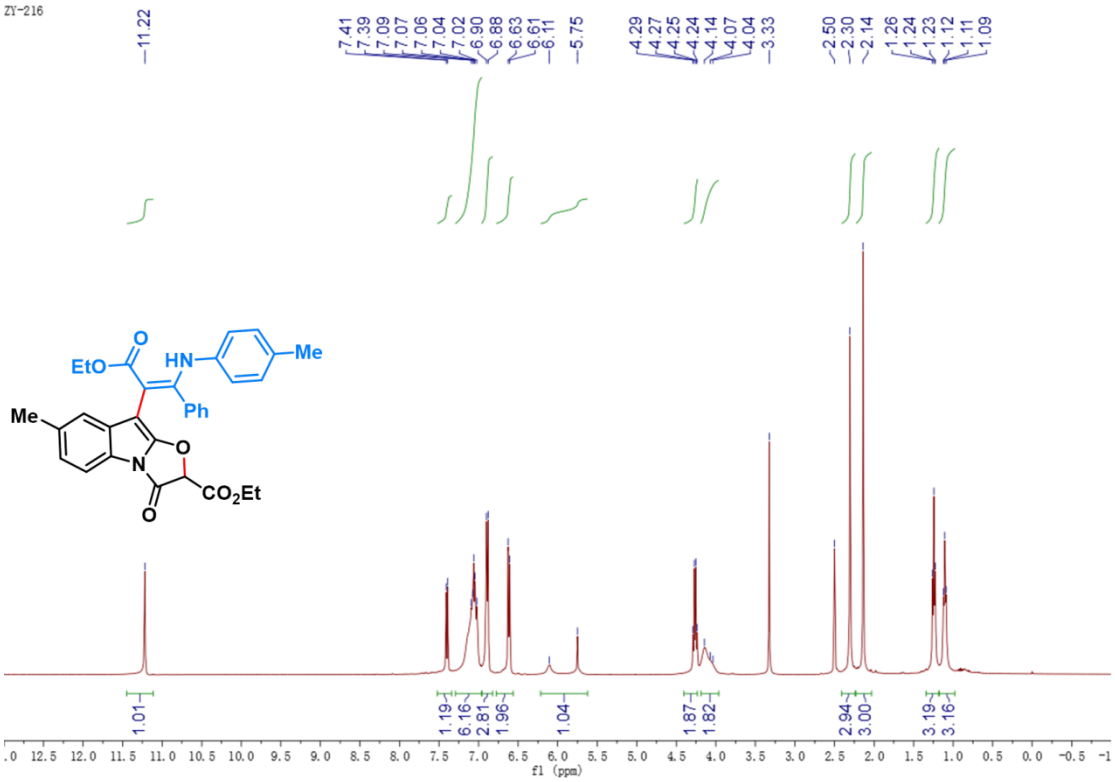
^{1}H NMR spectra of **5b**



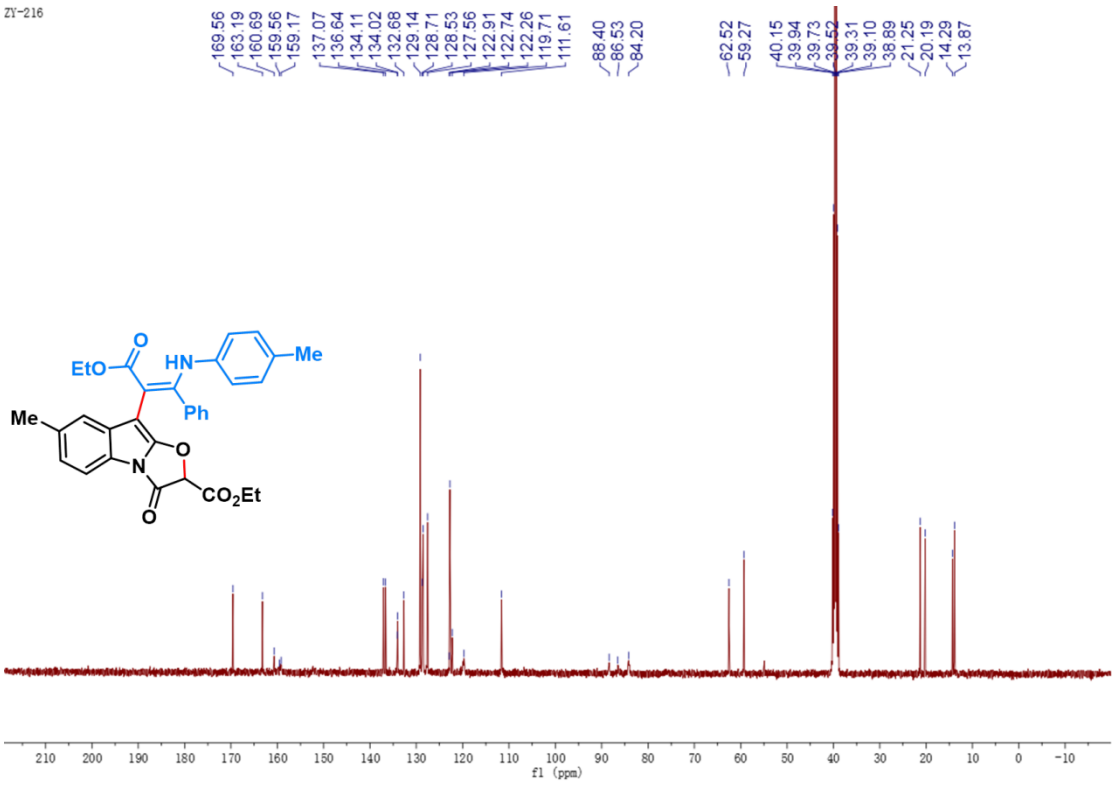
^{13}C NMR spectra of **5b**



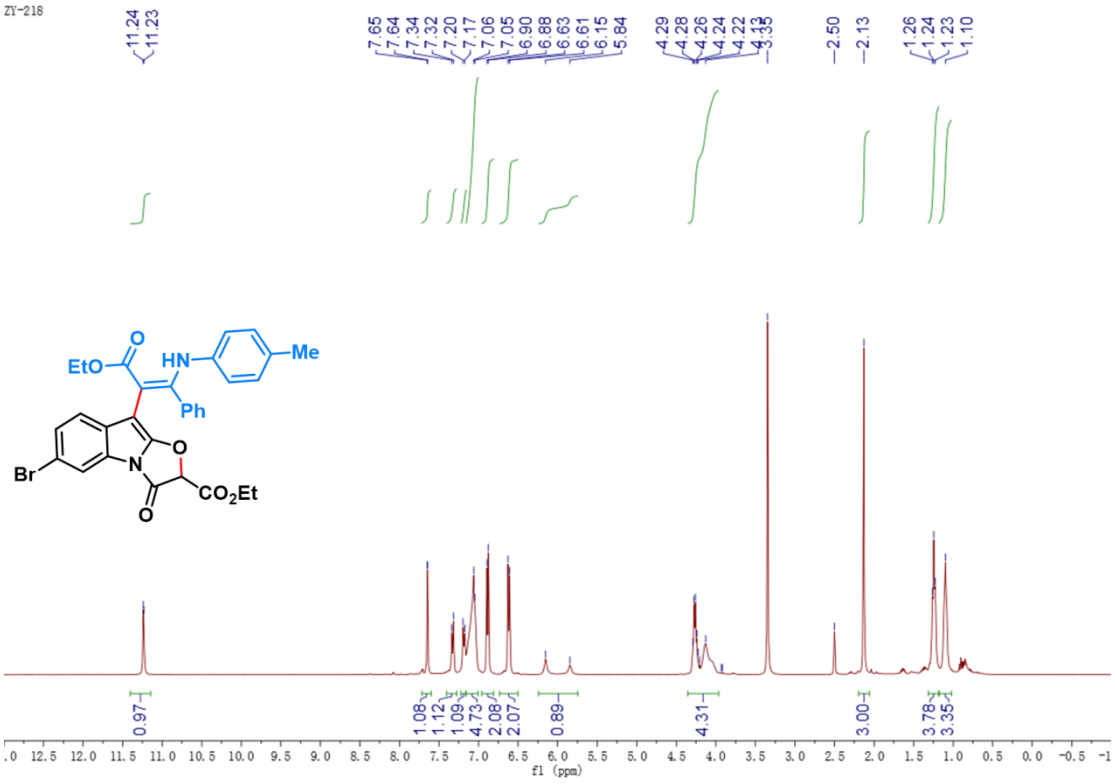
^{1}H NMR spectra of **5c**



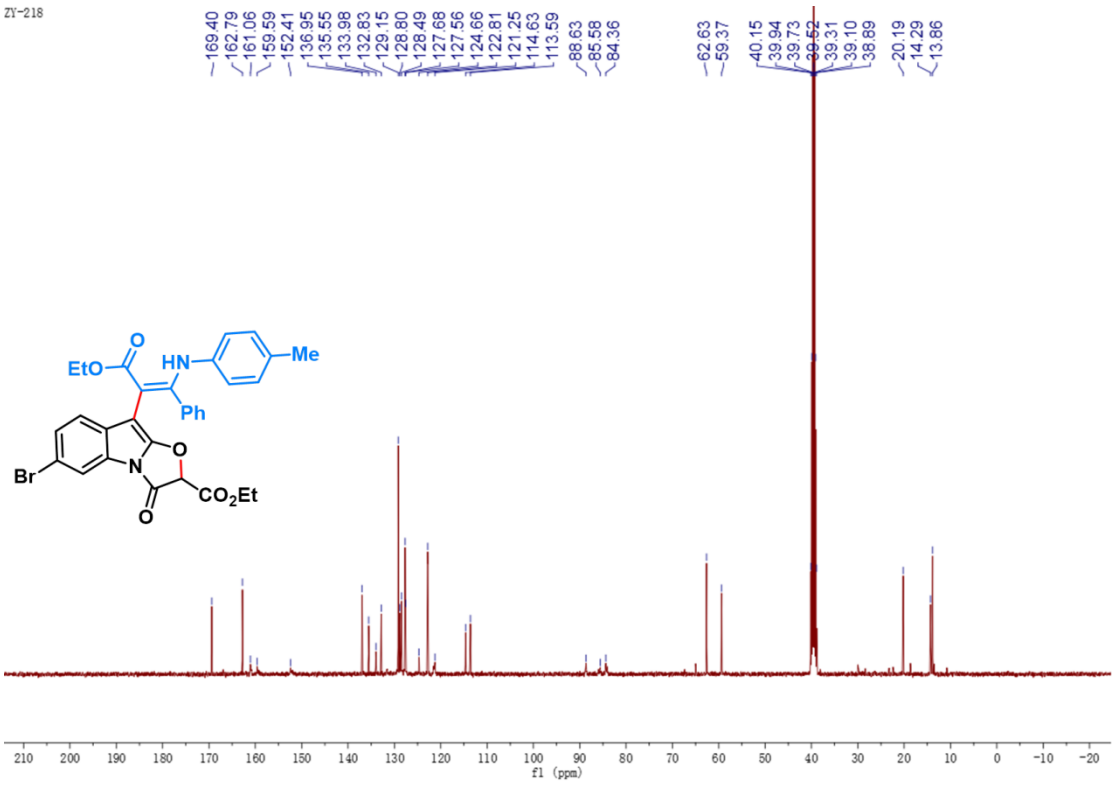
^{13}C NMR spectra of **5c**



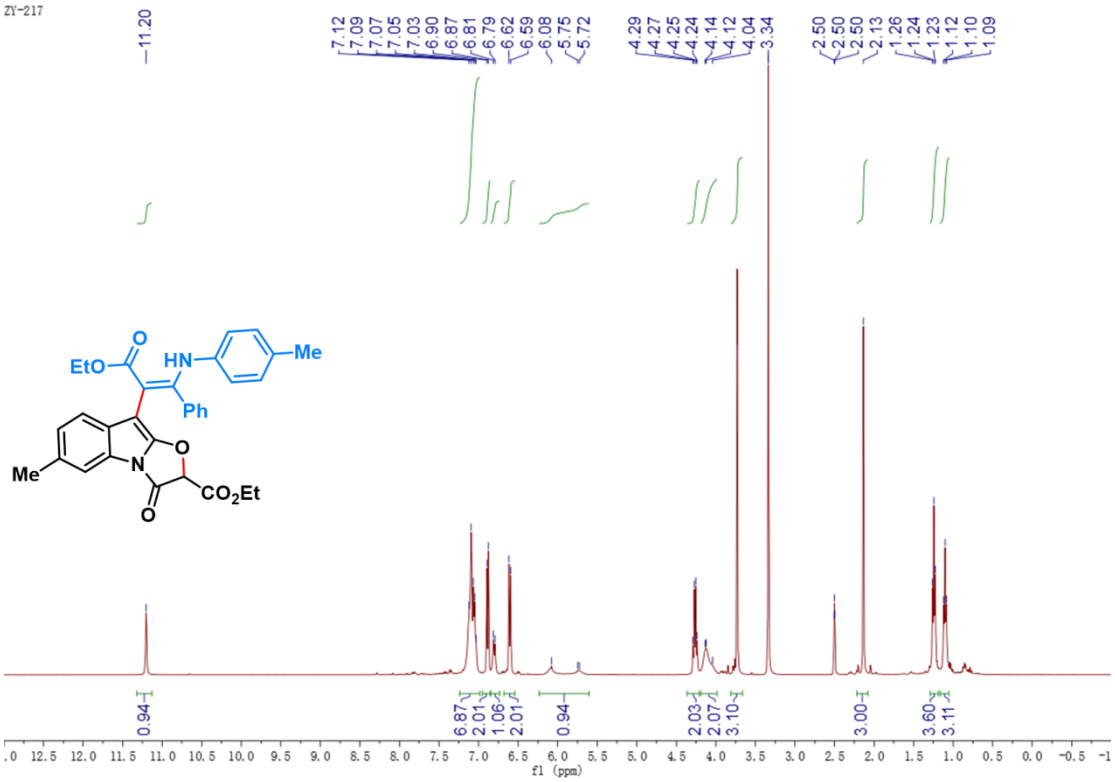
^{1}H NMR spectra of **5d**



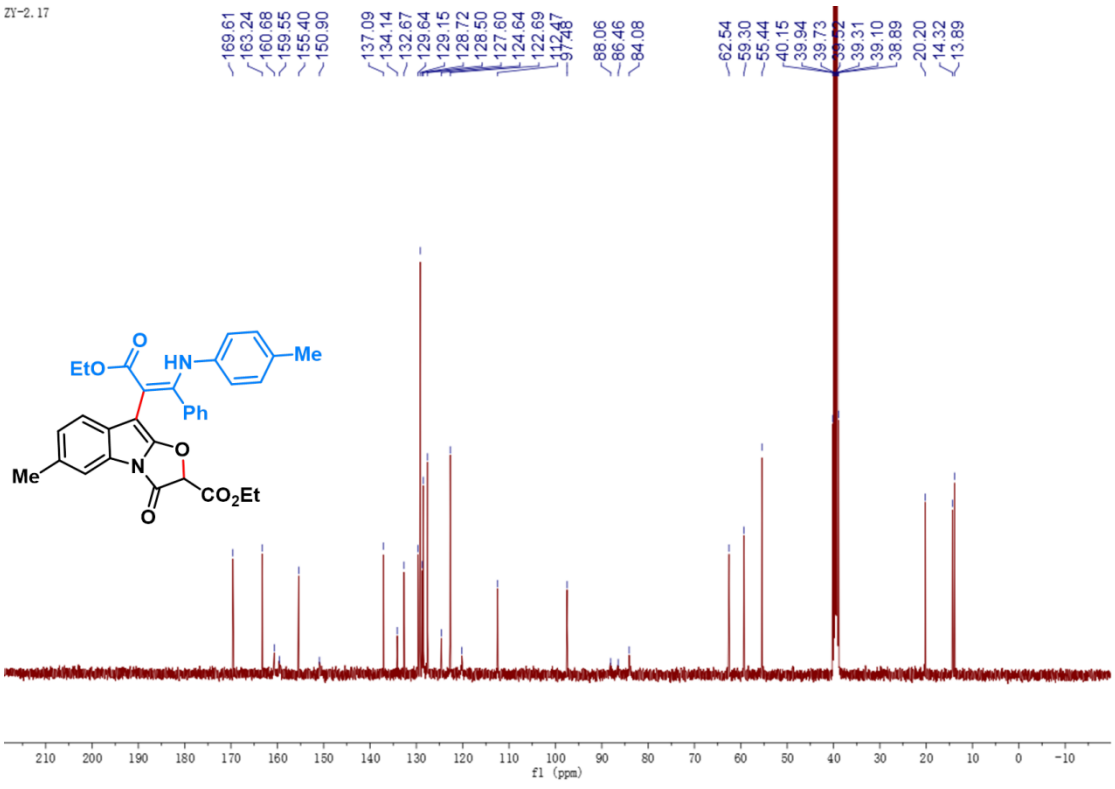
^{13}C NMR spectra of **5d**



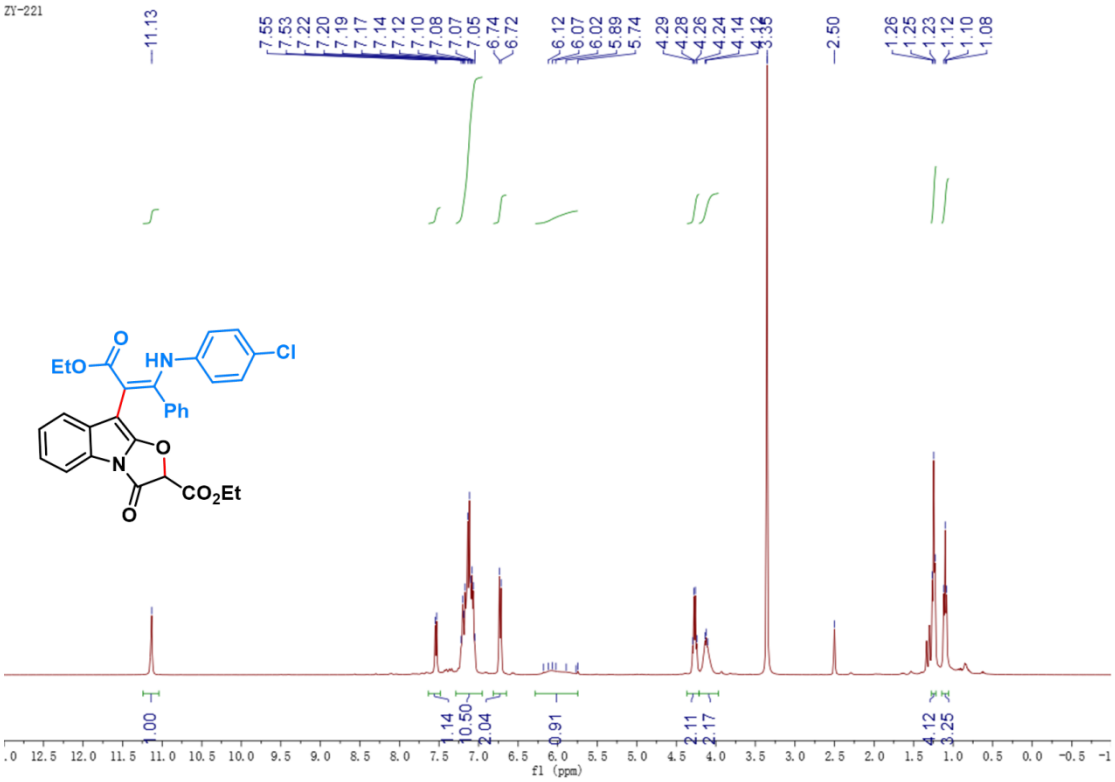
^{1}H NMR spectra of **5e**



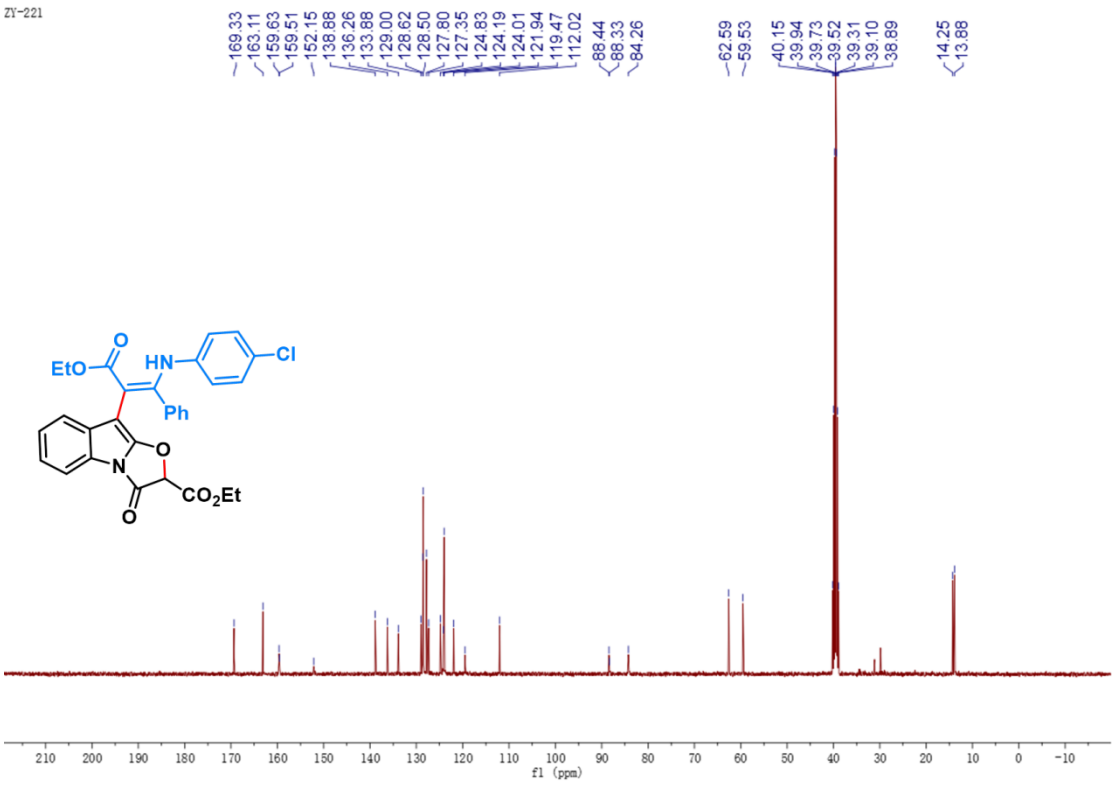
^{13}C NMR spectra of **5e**



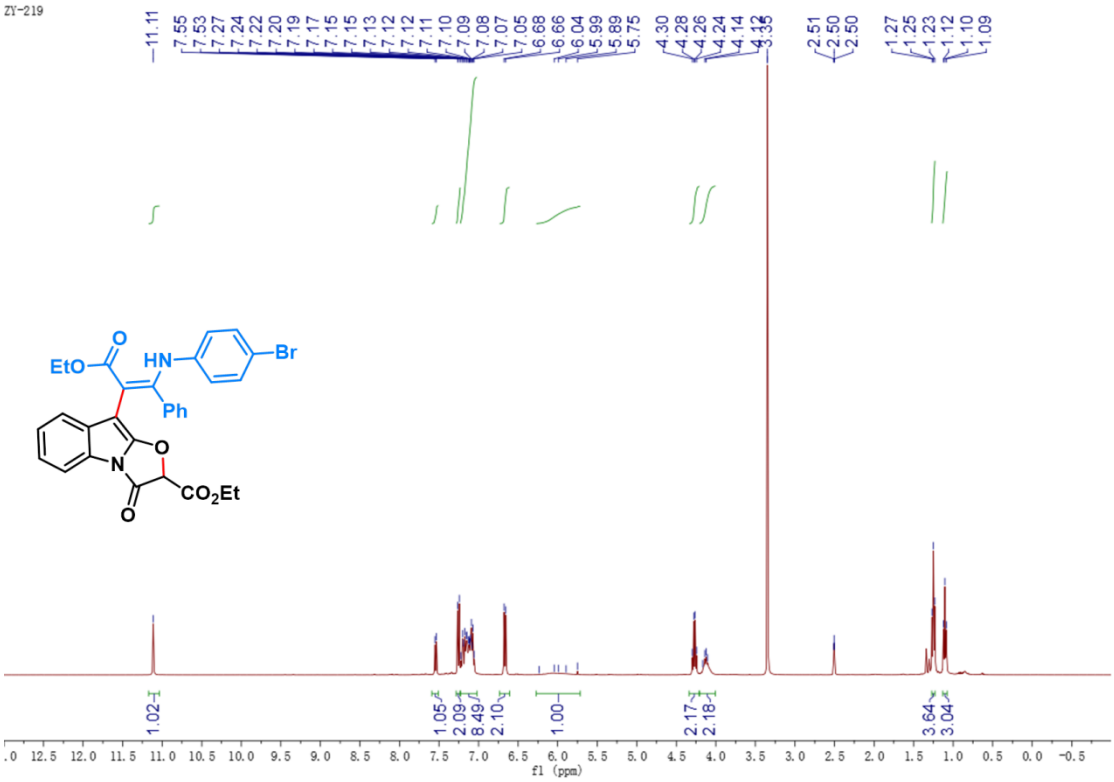
^{1}H NMR spectra of **5f**



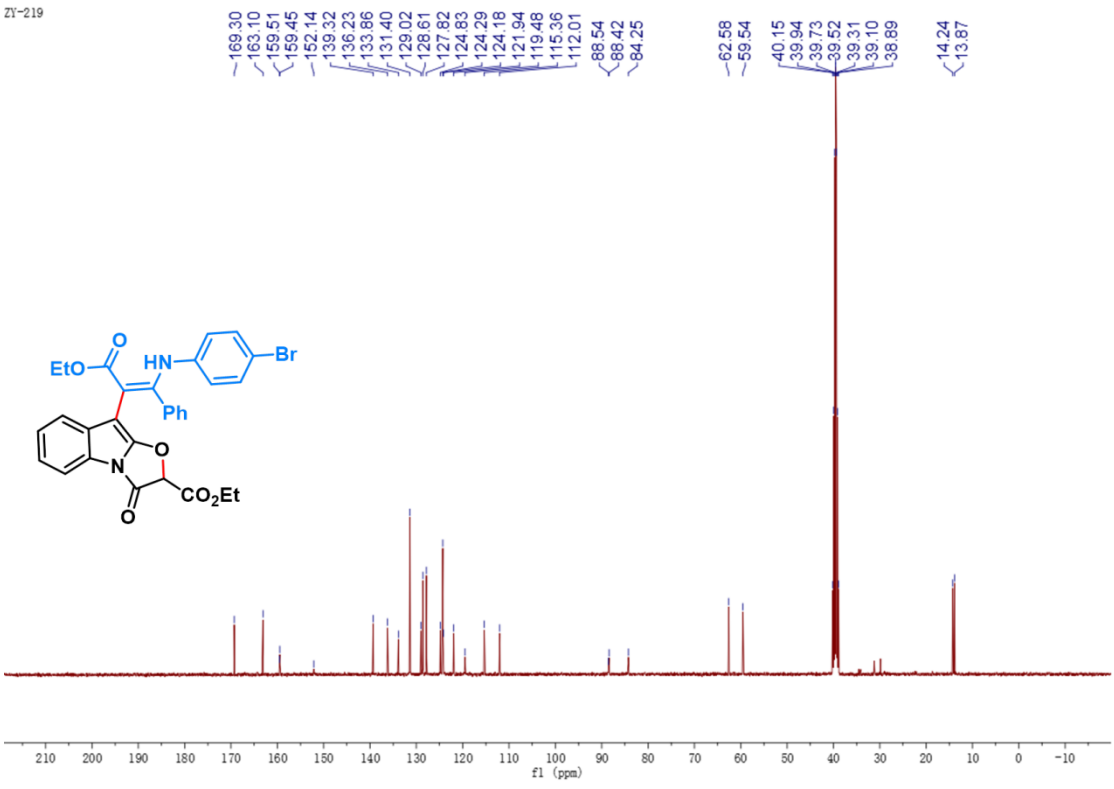
^{13}C NMR spectra of **5f**



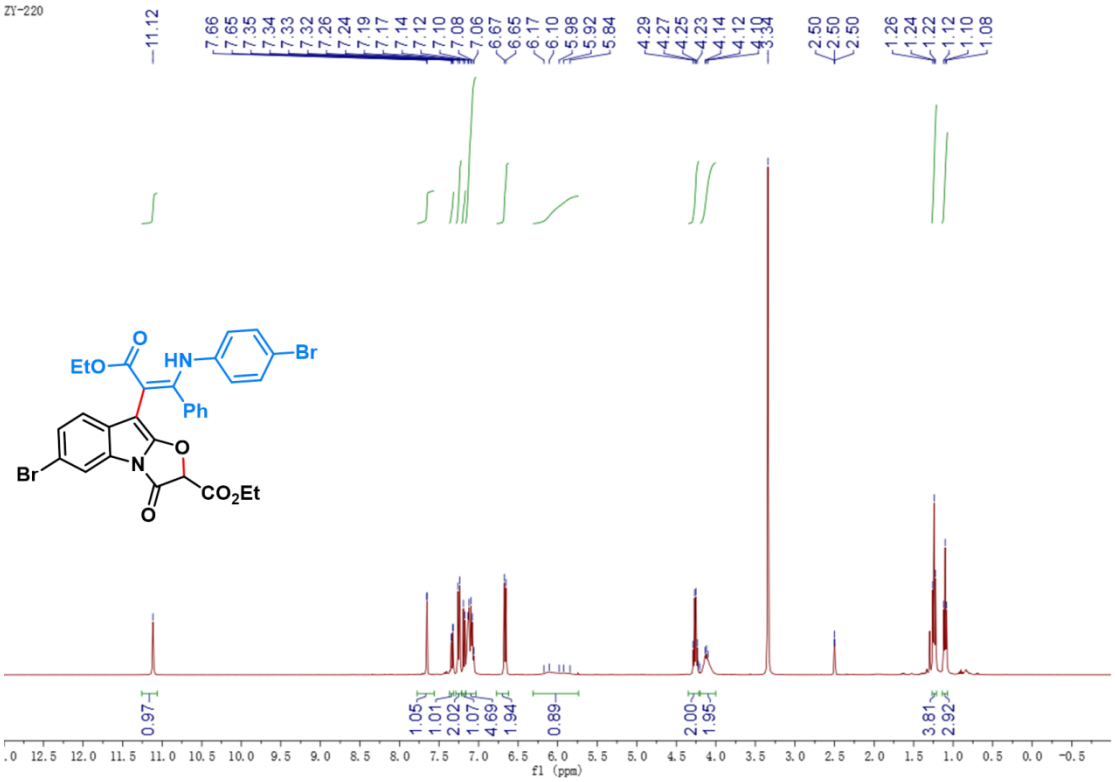
^{1}H NMR spectra of **5g**



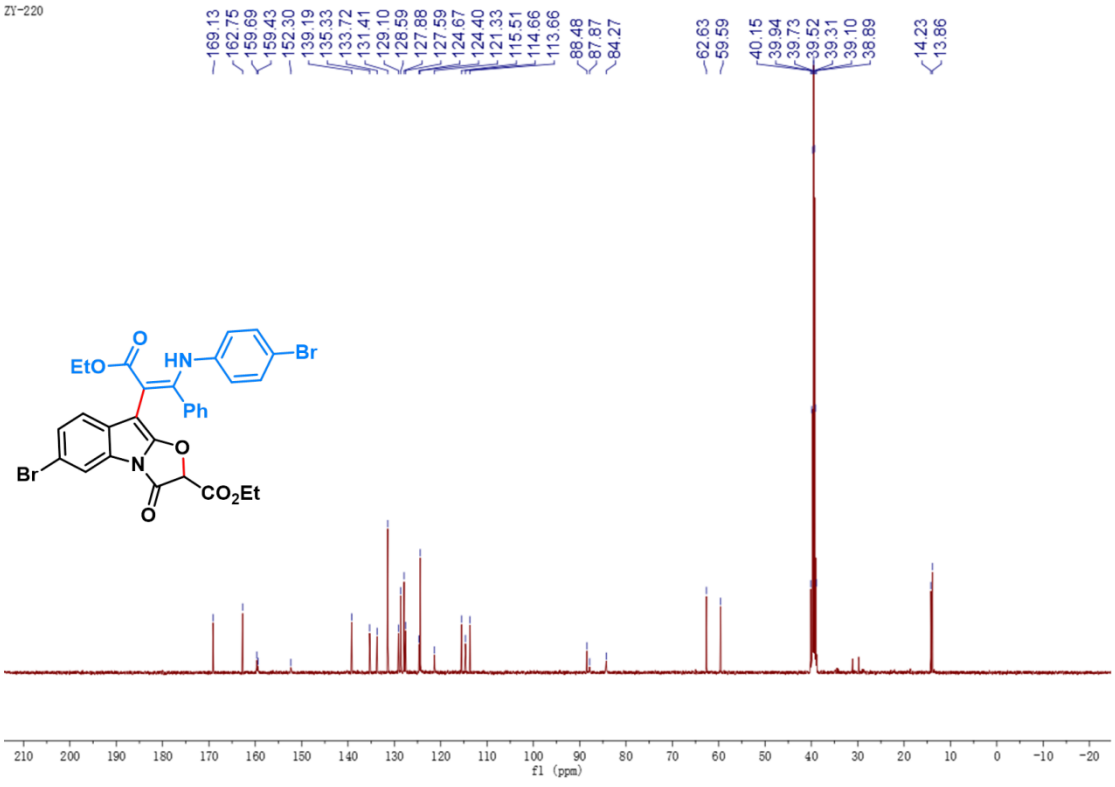
^{13}C NMR spectra of **5g**



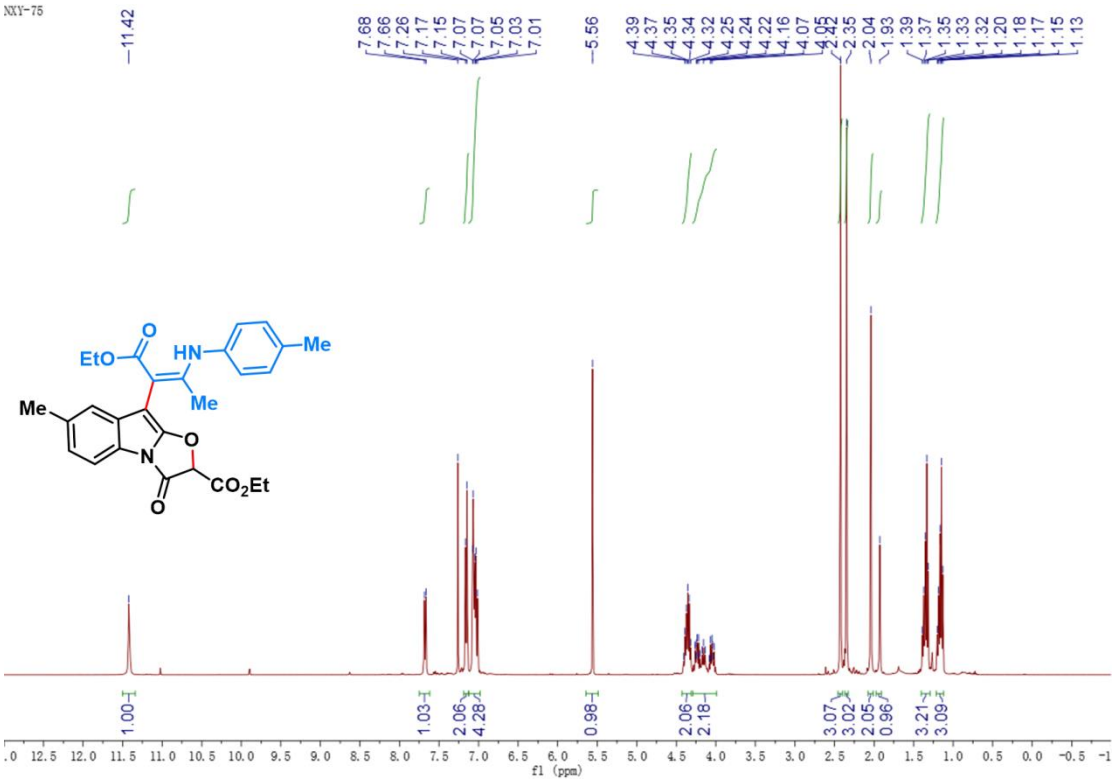
^{1}H NMR spectra of **5h**



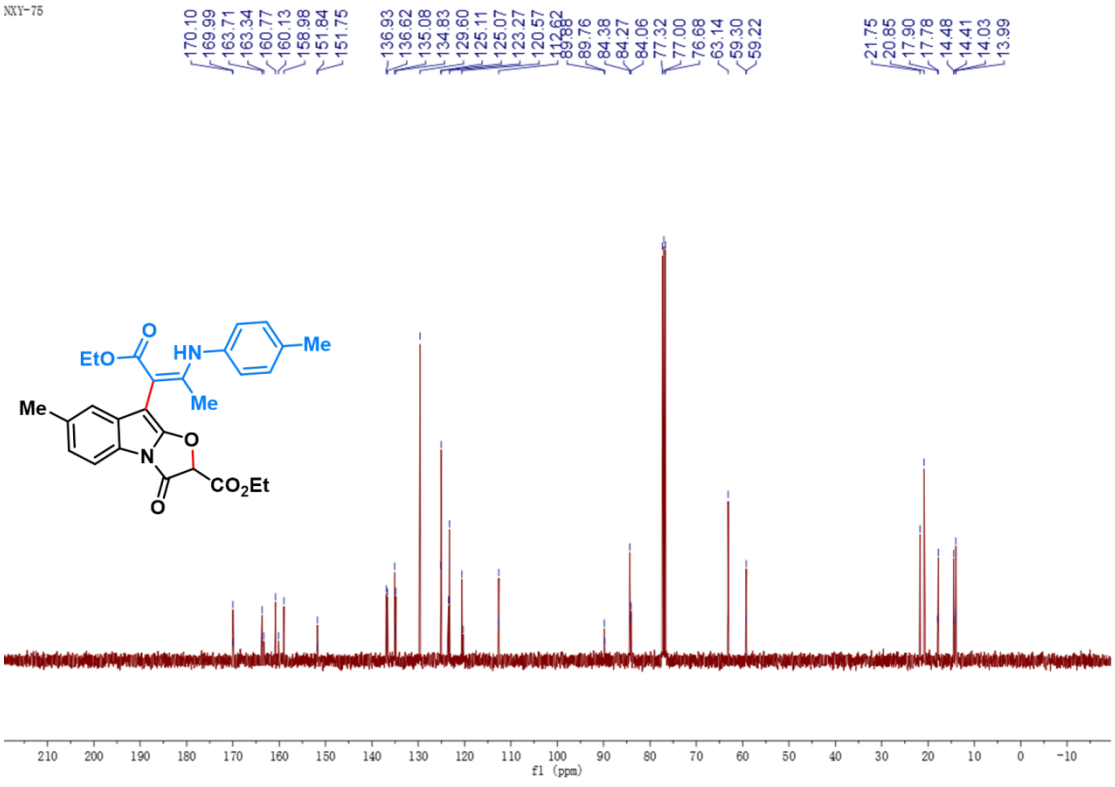
^{13}C NMR spectra of **5h**



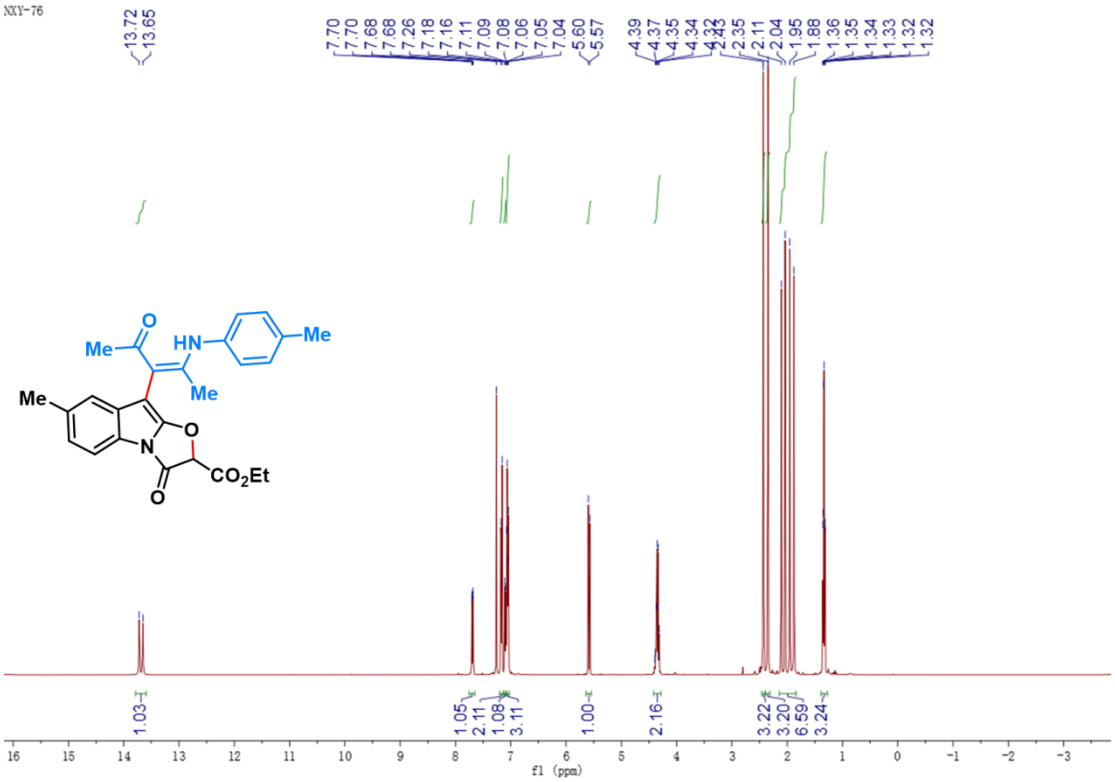
^{1}H NMR spectra of **5i**



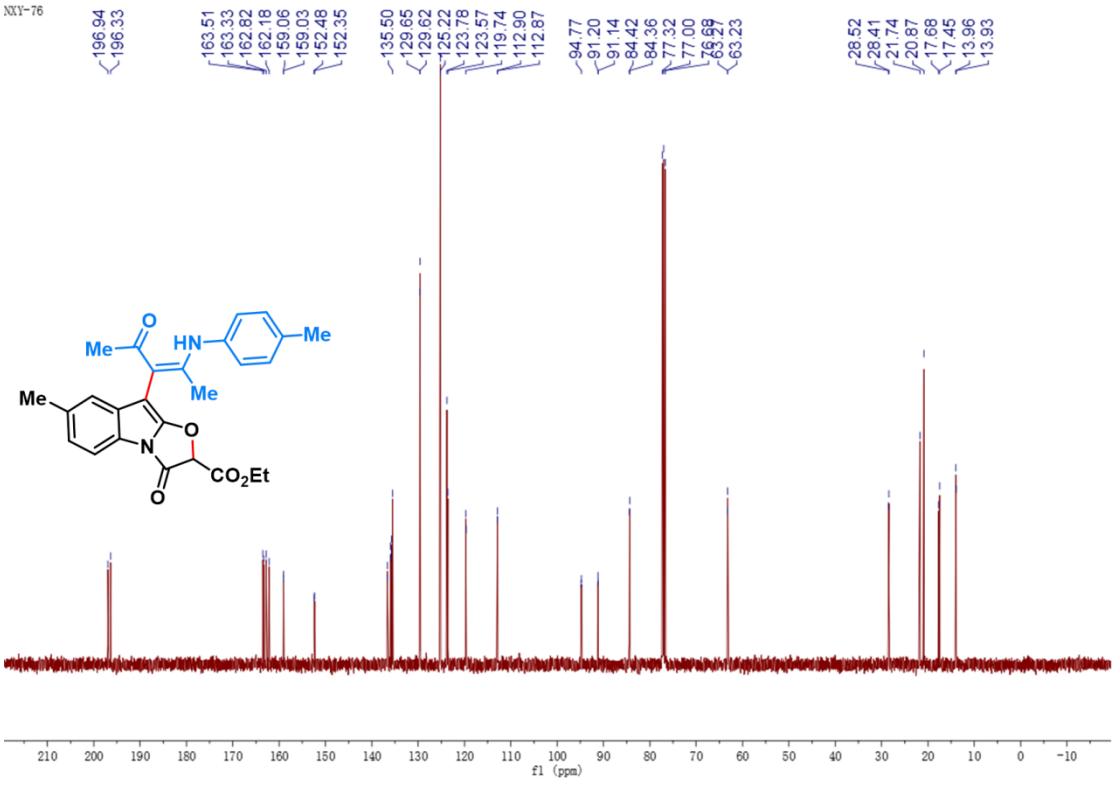
^{13}C NMR spectra of **5i**



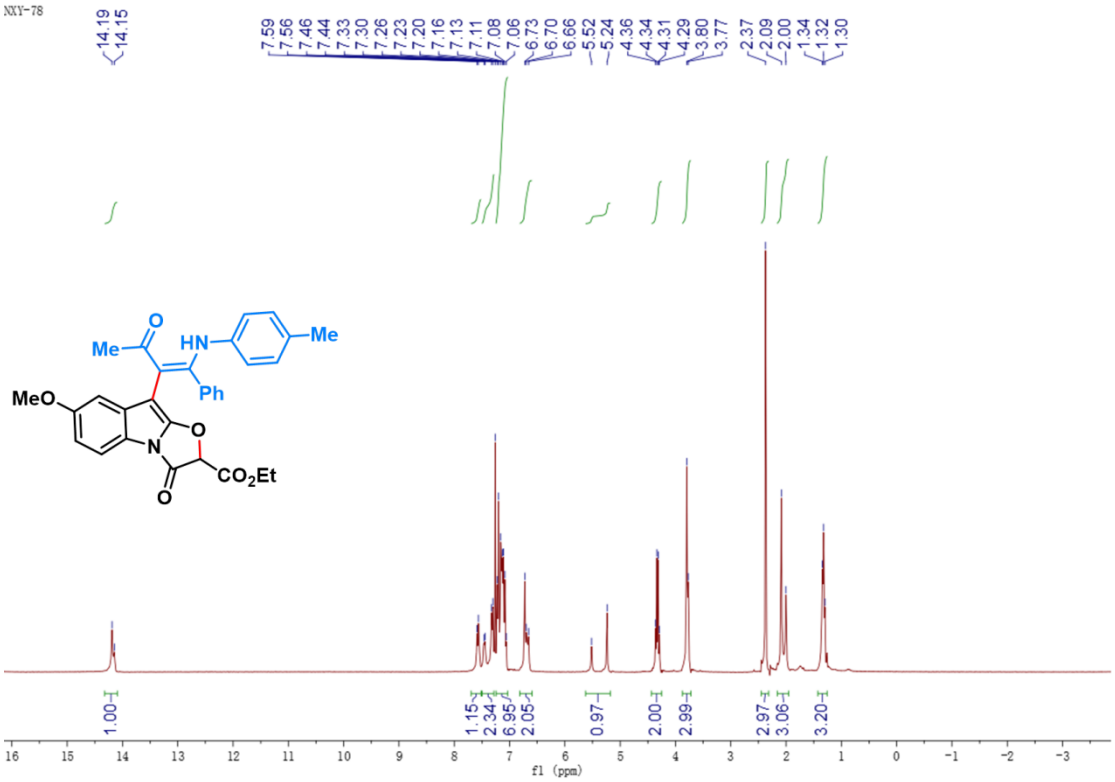
^{1}H NMR spectra of **5j**



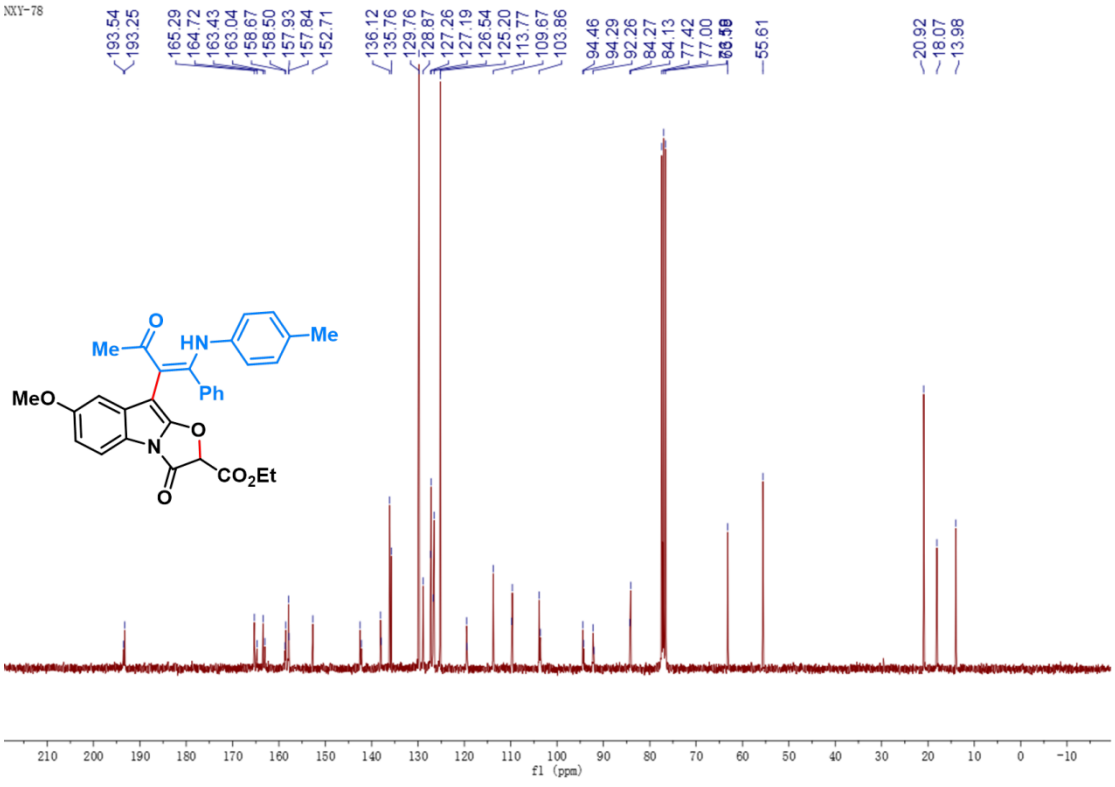
^{13}C NMR spectra of **5j**



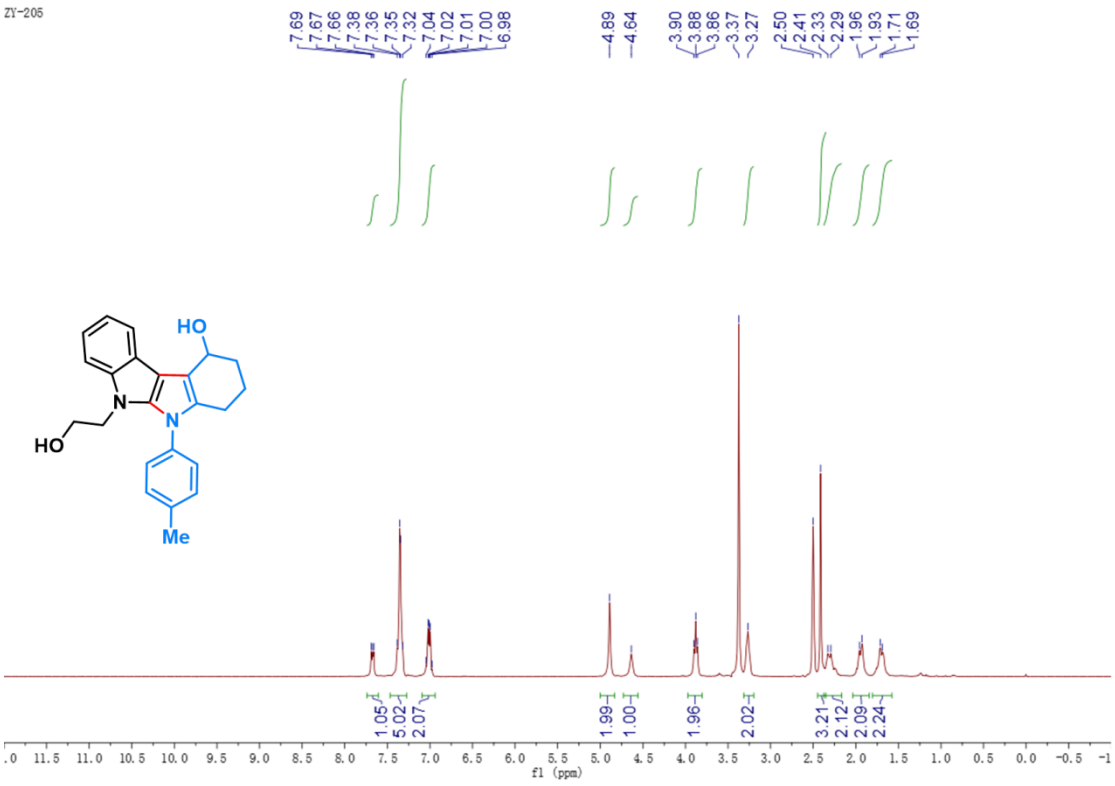
^{1}H NMR spectra of **5k**



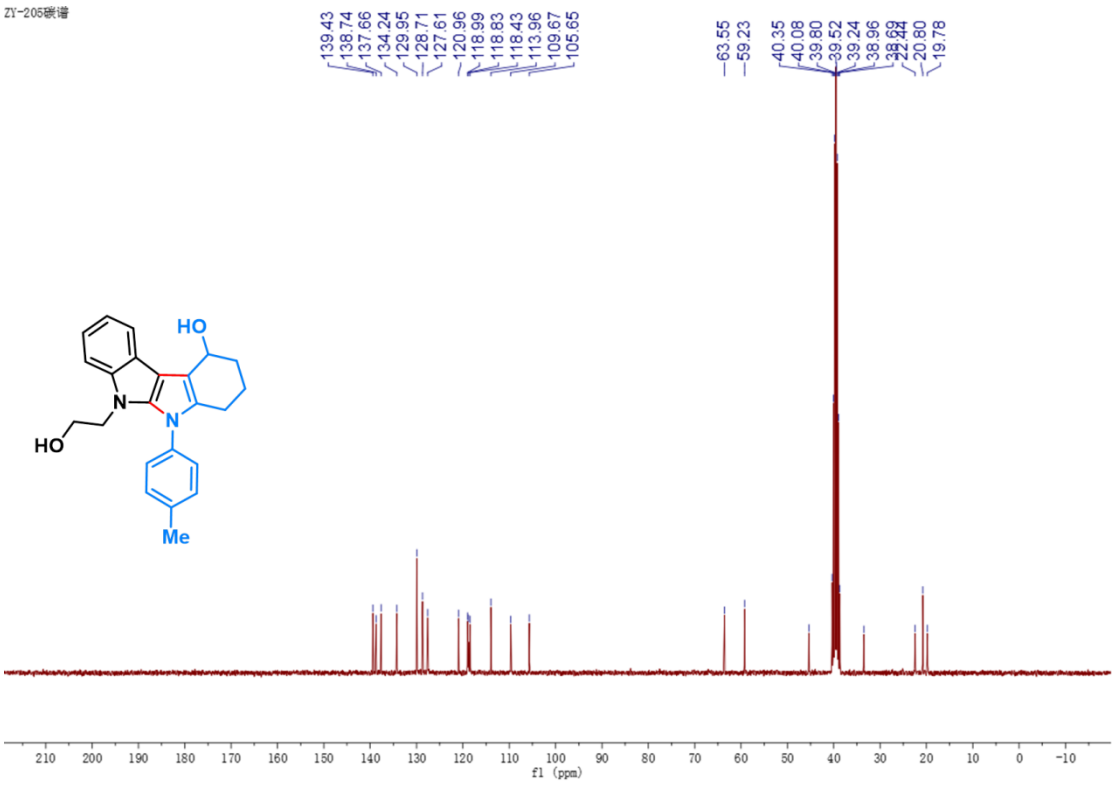
^{13}C NMR spectra of **5k**



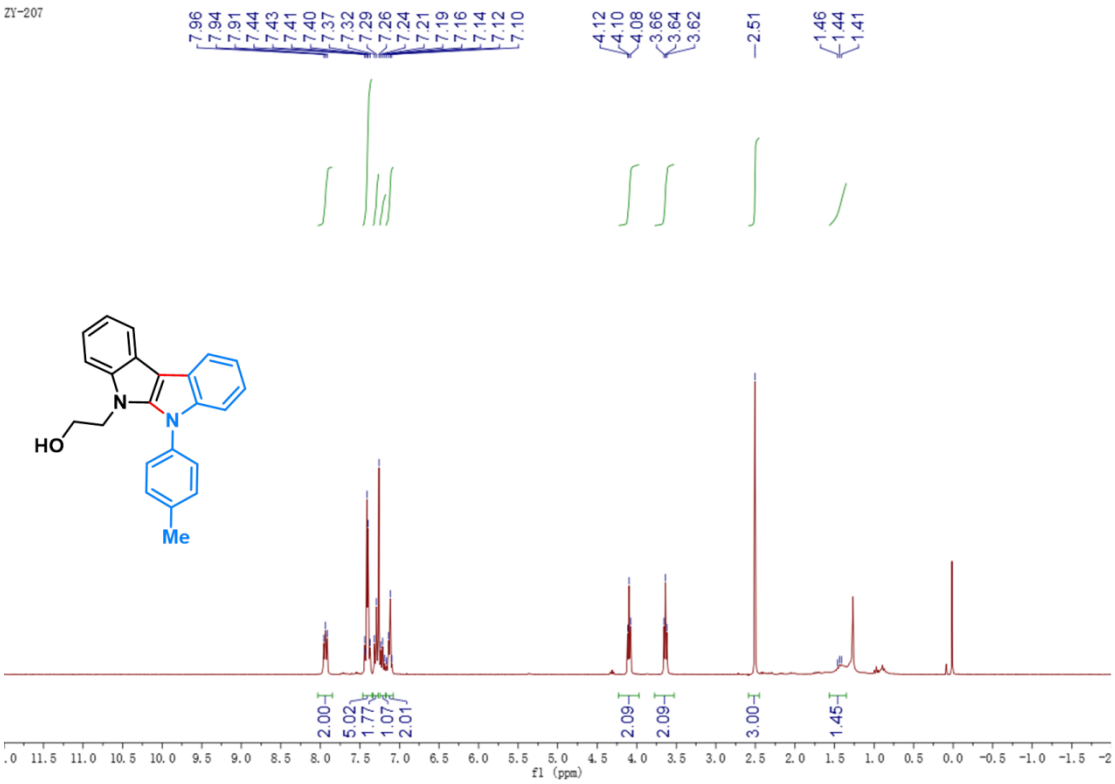
^{1}H NMR spectra of **6**



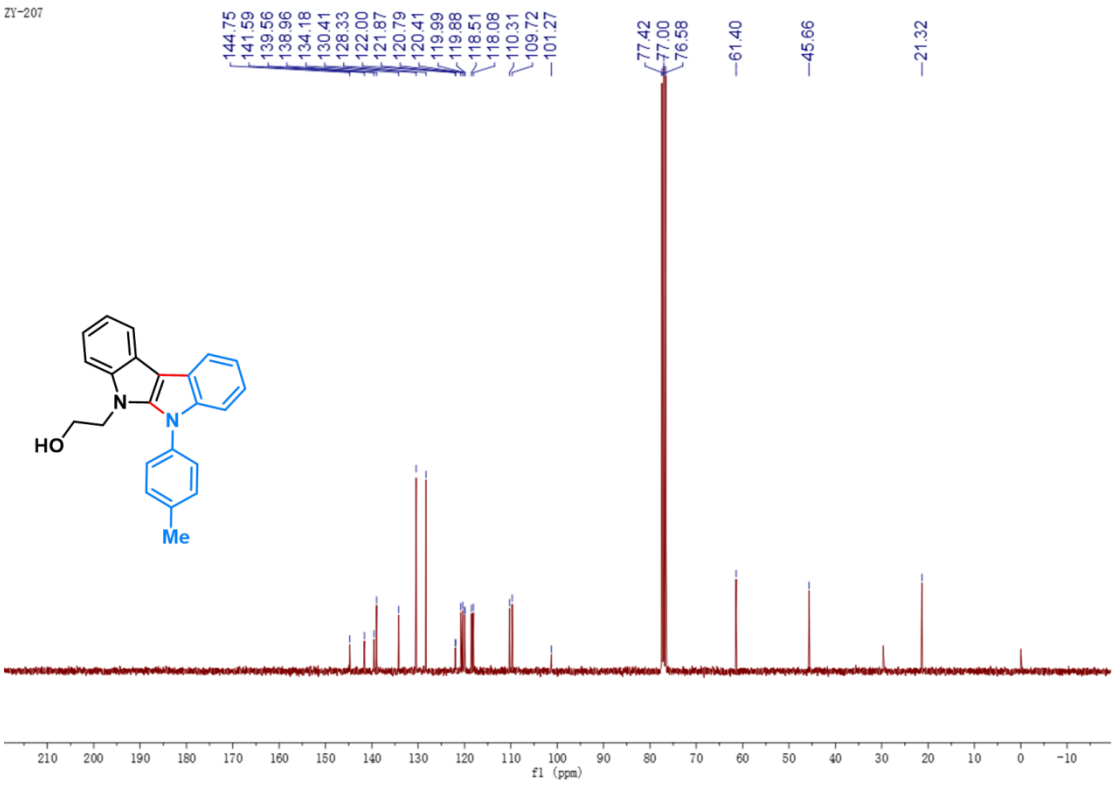
^{13}C NMR spectra of **6**



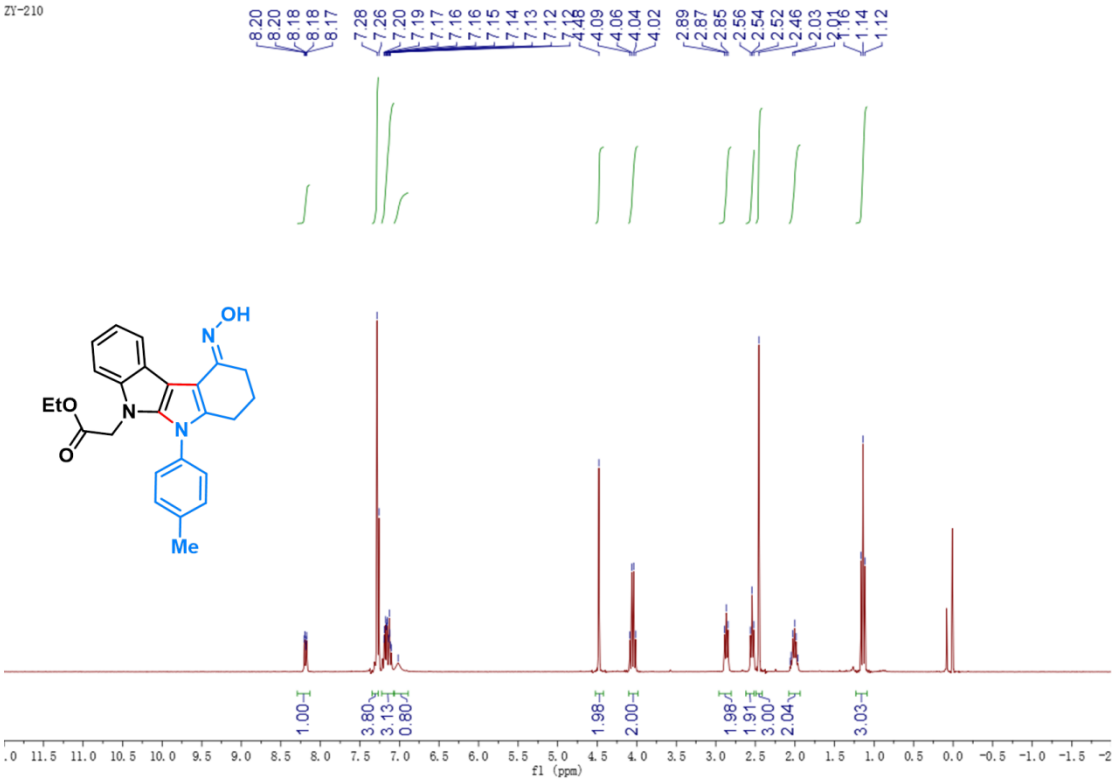
^{1}H NMR spectra of **7**



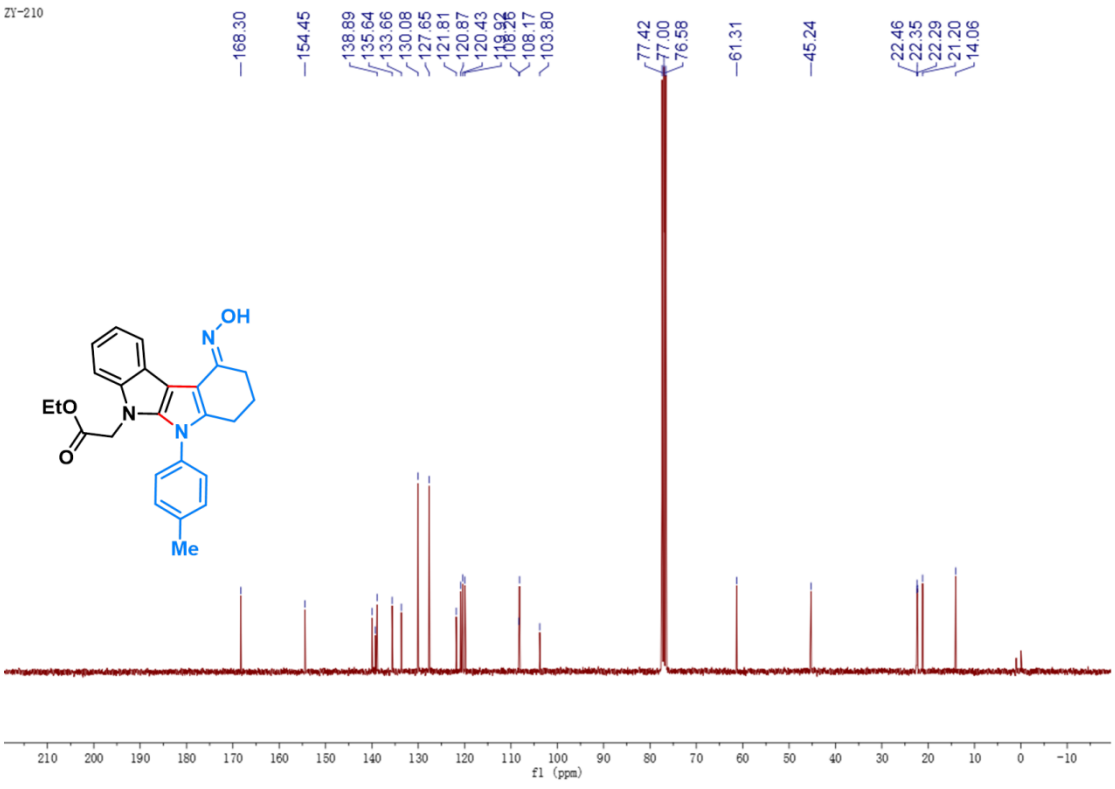
^{13}C NMR spectra of **7**



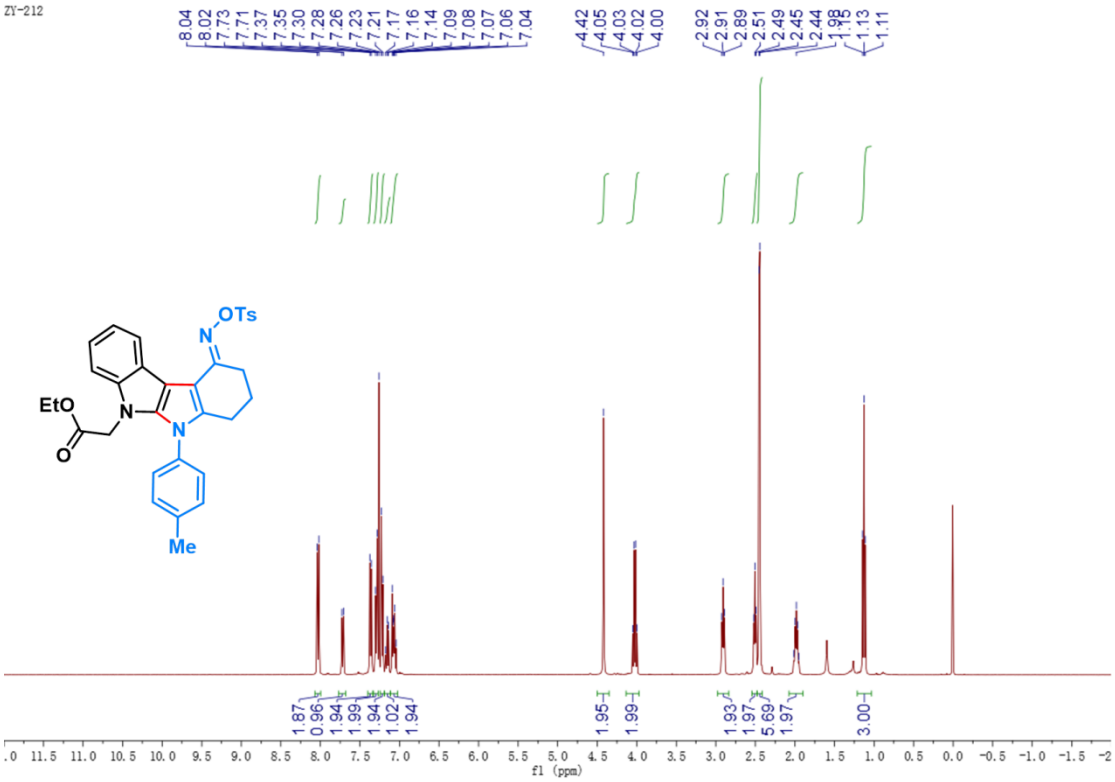
^{1}H NMR spectra of **8**



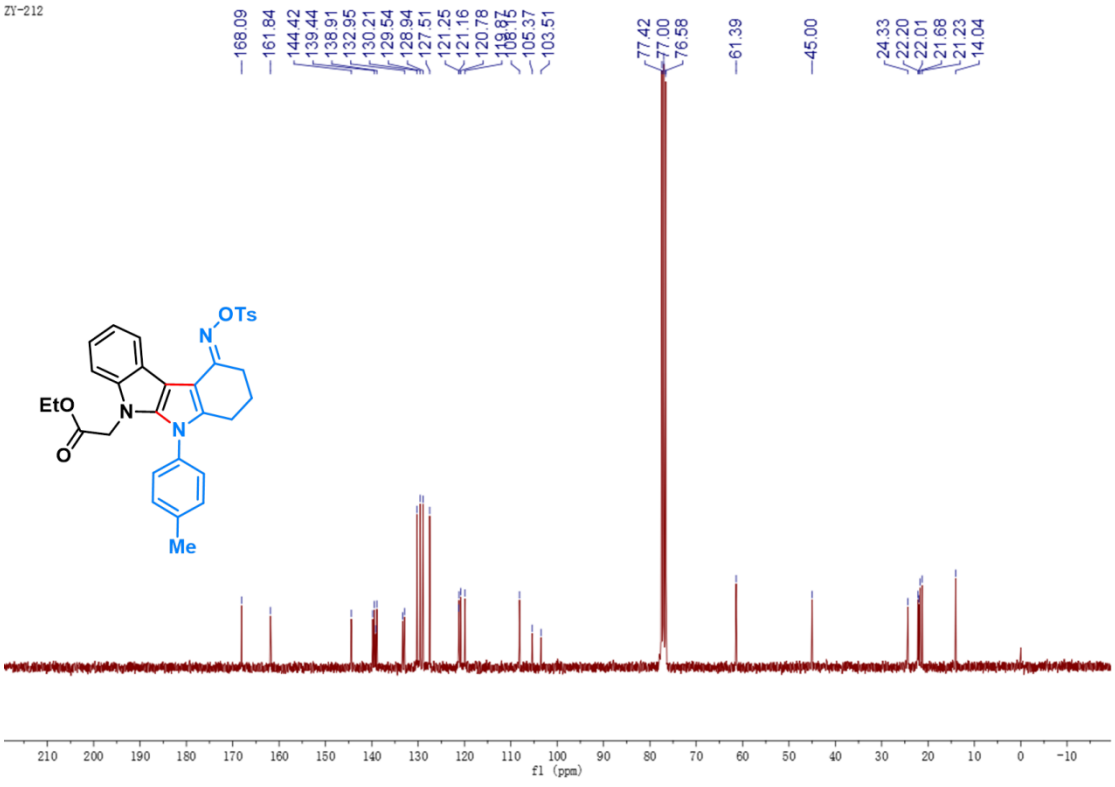
^{13}C NMR spectra of **8**



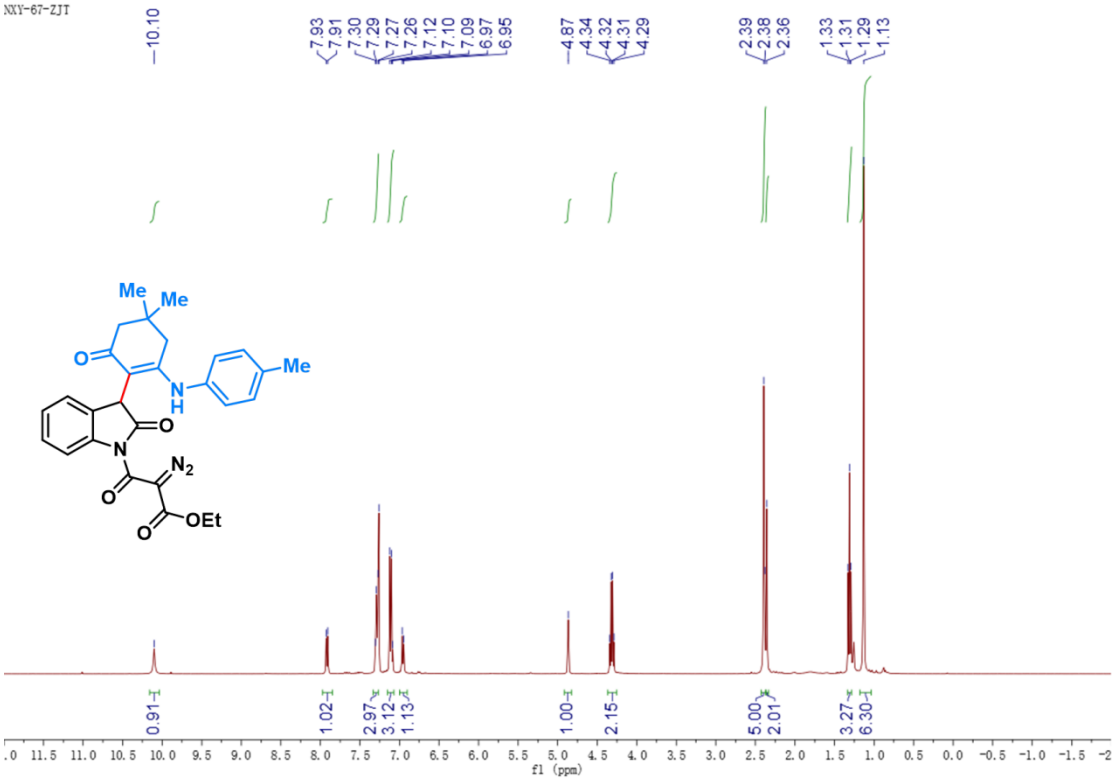
^{1}H NMR spectra of **9**



^{13}C NMR spectra of **9**



^{1}H NMR spectra of **Int-E**



^{13}C NMR spectra of **Int-E**